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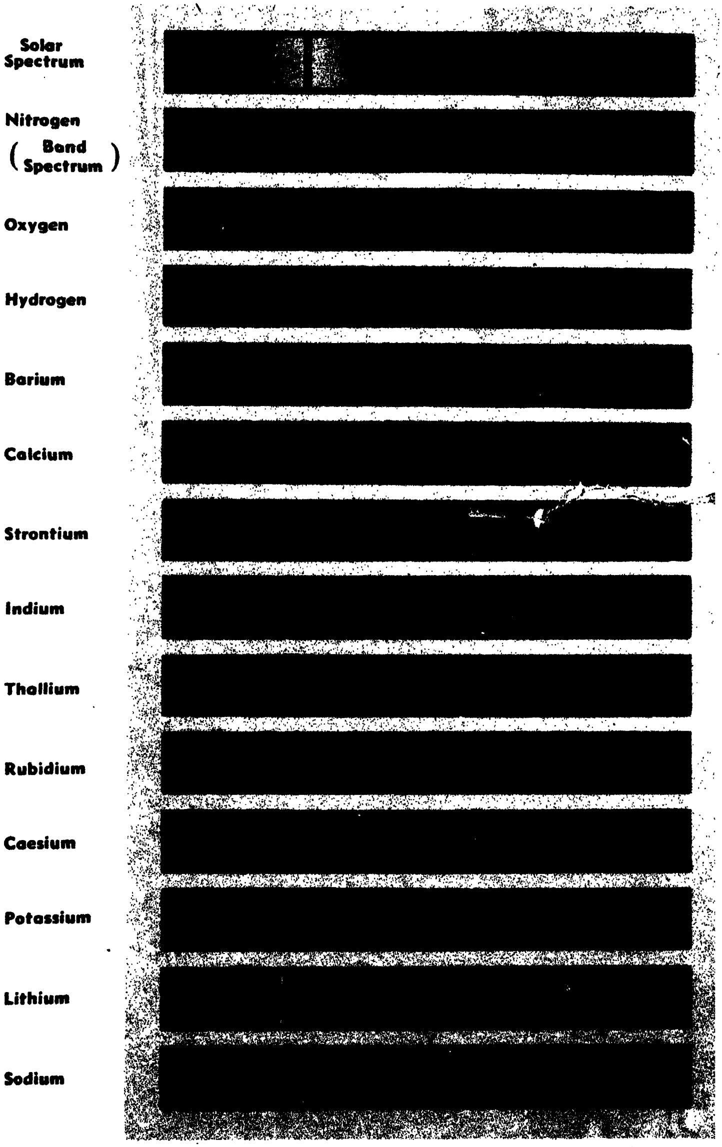

# AN INTRODUCTION TO
# GENERAL CHEMISTRY

BY

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AND

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*SECOND EDITION—SEVENTH PRINTING*

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*Happy the man who, studying nature's laws,*
*Through known effects can trace the secret cause.*
—*Vergil*

*Say not "this is the truth" but "so it seems to me,*
*to be, as I now see the thing I think I see."*
—*Anon*

# PREFACE

Like a menu with its promises of tasty dishes, this preface might intimate a survey of the fascinating discoveries of the past decade: synthetic textiles, plastics, hormones, vitamins, rubber and gasoline, and the amazing researches which have transmuted the chemical elements, and tapped the energy within the atom.

## TO THE STUDENT

But chemistry is not all so exciting as this. Before you lies the laborious task of mastering the chemical principles and facts which govern these astonishing transformations. The awakening of the layman to the importance of sober scientific research makes it wise to encourage this research attitude in the pages which follow. You will learn how the spirit of research has inspired great men to make it their life-work; you will learn of the rise and fall of important theories, and how much of what we accept today will be false tomorrow. You will learn how tediously the scientist must labor, in building up a body of substantial facts.

Make this textbook a reference book. Long after you have finished this course, you will find the **bibliography**, pages 751–765, a stimulating guide to information written by scientific pioneers about their own discoveries. Also, you may refer to the **statistics** of mineral resources and products, compiled chiefly from the U. S. Bureau of Mines *Minerals Yearbook* (*e.g.*, Table 94, page 483); and to the **uses of compounds**, tabulated at the end of several chapters (*e.g.*, pages 405–406). Finally, cultivate an ability to compose **question outlines**, similar to those following each chapter. Learn to reduce a mass of scientific details to an organized plan. This is most important.

Matter printed in smaller type is to be omitted, at the option of the teacher. Also, the list of materials in each Demonstration is information for the teacher, and may, in substance, be disregarded.

## TO THE TEACHER

Professor Foster's reputation as a scholar in the historical field reflects itself in the pages of his textbooks. In the present revision, his historical approach has, therefore, been carefully preserved. Also, the space devoted to each topic is essentially that of previous editions.

Two hundred **lecture demonstrations** are prefaced with lists of materials for their performance (*e.g.*, Demonstration 65, page 222). By this arrangement, the assembling of material for the lecture table may be left to a student or lecture assistant.

**Smaller type** has been used to segregate material which would normally be omitted in an elementary course: advanced topics (*e.g.*, pages 452–455), technical descriptions of industrial equipment (*e.g.*, page 474), and items of passing historical interest.

There are a number of **newer approaches.** For the inclusion of these the reviser's sole, but irrefutable, defense is their satisfactory use for over a decade in his own classes. These newer concepts include the use of potential energy curves for visualizing the role of energy in chemical reactions (pages 234–240), the presentation of energy levels and the Pauli exclusion principle to more advanced classes (pages 315–318), and a statement of the proton transfer concept of acids and bases (pages 278–283). Since the Brønsted system has not yet been wholeheartedly adopted into the chemical family, it is formulated as footnotes, while the Arrhenius theory is employed in the body of the text. Finally, the teacher will find that the metals are presented before the non-metals. The writer has never detected any confusion arising from this arrangement; and certainly the treatment of the groups of the Periodic Table in logical sequence has much to recommend it.

The chapters on acids, hydroxides and salts furnish sufficient background for the chapters on physical chemistry, which precede the study of the periodic table. For elementary classes teachers may prefer to reverse the order and present the periodic table first. Such a rearrangement, with chapters VIII–XI and XIV–XX placed after chapters XXI–XL, has been tested by actual class use of the galley proof, and found a satisfactory alternative.

## AND TO OTHERS

To the many people who have assisted in this revision thanks are due: in particular to Mr. Cushing Davis and to Professor Earle R. Caley, who ably criticized the whole of the manuscript; to Miss Helen Foster and a number of the writer's associates at Princeton; to the industrial firms who kindly furnished photographs and criticized the factual material; and, finally, to several hundred undergraduates at Princeton who used and criticized the galley proofs during the past year.

HUBERT N. ALYEA

Princeton, New Jersey,
July, 1941

## FROM THE PREFACE TO THE 1931 EDITION

This text-book is the result of much experience in teaching elementary chemistry to large classes of college students.

Since chemistry is a growing science, it is necessary from time to time to revise its subject matter. The cordial reception given *Introduction to General Chemistry* now makes it possible to take advantage of the criticisms and suggestions of teachers in other institutions.

The text-book is intended primarily for college students beginning the study of chemistry and for classes composed of beginners and of those who have had a high-school course in the subject.

As the result of much experience in teaching, the author is of the opinion that a course in General Chemistry should include some of the history of the science. The historical introduction has been somewhat extended; also portraits and short biographical sketches of some of the most eminent chemists have been included.

It is believed that the text-book contains numerous aids to good teaching. Generous use is made of various styles of type in order to emphasize very important facts and principles as well as to present some material of less importance which should be included in the text.

WILLIAM FOSTER

Princeton University
March, 1931

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# PART I: INTRODUCTION

The Rise of Chemistry

Elements, Compounds and Mixtures—the writing of chemical equations

Water and Its Constituent Elements

# CHAPTER I

## HISTORICAL INTRODUCTION

**1. Chemical Industry.**—Out of the test-tube has come the civilization of the twentieth century. Glance about us, and nearly everything upon which the eye falls bears witness to the activities of the chemist. Those huge chemical factories scattered about the country are creating a civilization of their own, a synthetic world which we have come to accept as our scientific heritage. It is a world unlike that of any other era; a world "of better things for better living" created from coal, air, water, limestone and oil. Man's ingenuity has bequeathed us a host of synthetic materials: rubber not only from the milky liquid furnished by the rubber tree, but from limestone or petroleum; not only glass from washing soda and sea-sand, product of an art practiced in antiquity by the Phoenicians, but a flexible, nonbreakable glass known to man for less than a score of years and manufactured from limestone, or oil, or skimmed milk; textiles not only from the hair of animals or the cotton plant, but from coal, from woods and grasses, from sand, from the scales of fish, from the curds of skimmed milk, from the oil of the whale, or from petroleum. These are a few of the products of modern chemical industry. In our study of the subject, we shall learn the chemistry of these substances, so that we may understand how the industrialist transforms a natural product into a valuable synthetic material. We shall learn how it has provided gasoline for our automobiles, gas to heat and light our houses, and fertilizers for the growth of plants; how we are able to produce ammonia, coke, tar and gas from coal, as well as the lovely colors called aniline from black coal-tar; how brick and pottery are produced from clay, and how iron is extracted from ores and changed into steel; how chemistry has provided modern explosives and made possible painless surgery by supplying ether, chloroform, ethylene, laughing gas, and a host of other anaesthetics.

Astonishing as these transformations may at first seem, magical though the changes appear, they are ofttimes simple chemical reactions which underlie the harnessing, by industry, of the forces and materials of nature in fashioning our test-tube civilization of today. We shall seek to replace the mystery of magic by the concepts of chemical change.

**2. Chemistry in Other Sciences.**—In addition to its service to industry, chemistry has become closely related to the other sciences; so much so that it is often impossible to define them sharply. The **astronomer** observes the color of light from a star, and from that deduces the chemical elements in the star. Copper in a hot star or a burning Roman candle alike gives off a greenish-blue light. The astronomer also infers chemical changes in the star by duplicating these reactions in the chemical laboratory. The **physicist** studying the transformation of energy and the action of matter, turns to chemistry to explain how energy may be converted into matter, and matter into energy. He taps the energy of the chemical atom. He utilizes and improves non-breakable lenses, neon and sodium lights, radio and thyratron tubes, tape-measures made of special steel which neither shrinks in cold weather nor expands in hot. The **geologist** studies the chemistry of the rocks, and of their formations. The **biologist** investigates the chemistry of life. The major contributions in this science today have been in the field of bio-chemistry. This is the science which has given us synthetic vitamins and hormones; and remedies for goitre, leprosy, diphtheria and scarlet fever. This is the field which has produced the powerful new drugs sulfanilamide, sulfapyradine and their derivatives; which, during the first years of their use in the United States (1939–40) cut deaths from pneumonia forty per cent.

**3. Pure Chemistry.**—In all of these branches of science, and beyond the realm of chemical industry, lies the domain of pure research. In our universities and in many of our industrial laboratories scientists are experimenting, testing, gathering data and interpreting those data; scientists, striving constantly to satisfy their own intellectual curiosity. To them, here is a universe to be examined, weighed and measured, and it is their task to examine, to weigh and to measure it. Why does iron rust, but gold not? What is light and fire? What is the chemical nature of important substances in the human body such as the male and female sex hormones? How does chlorine kill germs in drinking water or bleach textiles? Why does salt become sticky in damp weather? There is no other man on earth quite as unique as the pure research worker. He is after the truth and truth only. He does not ask whether what he seeks is useful or useless, whether it is beautiful or ugly, whether it is just or unjust; merely, is it the *truth?* Does it represent the facts? And to this he pledges his life, as Scheele the great Swedish chemist said,

"It is the truth alone that we desire to know and what a joy there is in discovering it."

Scheele's method was the method of experimentation. It has been the basis of most real progress in science during the past hundred and fifty years. We owe this remarkable advance to the well-equipped laboratories which have been dedicated to experimentation; to the ever-expanding facilities opened up to the research worker in the past few years; to the attention which thinkers have given to the making of accurate observations and the impartial recording of facts. These are all attributes which the student may profitably imitate in his own work.

In ancient times, however, experimentation was not in vogue. There have been, of course, great experimentalists throughout the ages of man, but in general men of education in ancient Greece did not perform experiments, for they considered it beneath their dignity. There was much speculation as to the nature of things, but the hypotheses advanced to explain phenomena were often extravagant. The love for experimentation took root during the intellectual Renaissance of the Middle Ages, and burst into full flower with the discovery of oxygen at the time of the American Revolution.

The story of the growth of chemistry has been the story of the rise of this experimental method, to which we shall now turn, and follow from its beginning.

## HISTORICAL

**4. Applied Chemistry in Egypt.**—When we attempt to find the meaning of the word "Chemistry," we are carried back to the most ancient peoples—to the very beginning of civilization. Scholars are not in agreement as to its meaning. Some writers hold that the word refers to the land of *Chemî* (Egypt), which was the cradle of chemistry; while others believe it to have been derived from a Greek word meaning a *mingling* or an *infusion*, for chemistry was at first the art of extracting the juices from plants for medicinal purposes. It is said, therefore, that chemistry originated in the temples where priests experimented in preparing medicines. In Biblical times, the women of the East used cosmetics, such as antimony trisulfide, for painting the eyebrows

(2 Kings IX. 30 and Ezekiel XXIII. 40). Good wine, salt and vinegar were not unknown to them. Excavations show that the Egyptians were acquainted with the working of gold, silver, copper, lead, and iron; that they understood the art of manufacturing pottery from clay; knew how to produce enamels, alloys, and artificial gems; and greatly developed the arts of dyeing and of embalming their dead. Inscriptions representing glass-makers plying their art have been unearthed in Egyptian monuments of the 11th dynasty, showing that considerable skill in glass-making was developed at least 2,000 years before the Christian era.

**Medicine** developed in the early history of peoples in response to their urgent needs. It has been called the foster-mother of many sciences. We can trace the origin of chemistry, anatomy, physiology, and botany in the records of Egyptian medical practice. The first physician of whom we have any record lived about 4500 years ago. His name was I-em-hetep (He-who-cometh-in-peace). Pictures of surgical operations, not later than 2500 B.C., have been found near Memphis. To find remedies for diseases the practitioner ransacked the resources of nature. Many data are obtained from the Ebers papyrus, largely a collection of prescriptions. Among the 700 recognized remedies are many familiar substances such as poppy-seed oil, castor-oil, gentian, sodium bicarbonate, antimony, and salts of lead and copper. As a prescription for baldness, the fats of the lion, hippopotamus, crocodile, goose, serpent, and wild goat, in equal parts, were prescribed.

Babylonia, too, had its applied chemistry. W. Libby says:

> "The **Babylonians** were a nation of agriculturists and merchants. . . . Belshazzar, the son of a Babylonian king, dealt in wool on a considerable scale. Excavation in the land watered by the Tigris and the Euphrates tells the tale of the money-lenders, importers, dyers, fullers, tanners, saddlers, carpenters, shoemakers, stonecutters, ivory-cutters, brickmakers, porcelain-makers, potters, vintners, sailors, butchers, engineers, architects, painters, sculptors, musicians, dealers in rugs, clothing and fabrics, who contributed to the culture of this great people. It is not surprising that science should find its matrix in so rich a civilization. . . ."

**5. Chemistry in Ancient Greece and Rome.**—These great nations of antiquity, however, failed to carry the sciences that arose in connection with their arts to a high degree of generalization. That was reserved for another people of ancient times, the **Greeks.** The Ionian Greeks were ruled less by fear than were the Egyptians and the Babylonians. The Ionians insisted that Nature was orderly and understandable. The Greek philosopher of the sixth century B.C., with mind freed from the bondage of mysticism and supernaturalism, with a love of knowledge for its own sake, and with a freedom of intellectual outlook hitherto unknown, sought for a rational and natural explanation of phenomena. But he did not experiment; it was undignified; it was something for his slaves to do. As a result his vast amount of speculation on the nature of things was often fanciful. A good illustration of this was his concept of matter. According to the doctrine of Empedocles (about 450 B.C.) and Aristotle (384–322 B.C.), matter was made up of four elements: Earth, Air, Fire and Water. Each of these signified certain characteristics and physical properties. Thus "earth" implied the properties of cold and dryness; "water," cold and moisture; "air," heat and moisture; and "fire," heat and dryness (Fig. 1). Presumably all matter was of one kind, and the wide variety of matter was thought to be due to the greater or less abundance of these four elements or principles. In addition to this material world, there was a divine spirit or essence, a fifth element or "quintessence," which pervaded all matter.

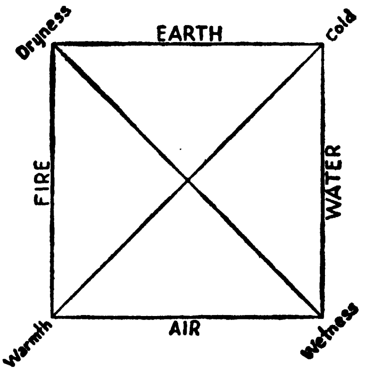

FIG. 1.

Aristotle was one of the few ancient thinkers who practiced the experimental method. At one time, aided by a grant from Alexander the Great, he had 100,000 men scattered throughout the Mediterranean basin collecting and classifying animal and plant life. Since he insisted upon the collection of facts, followed by accurate interpretation of the data collected, he is recognized as an originator of the scientific, experimental method.

After the conquest of Egypt in 332 B.C., Alexander the Great founded the city of Alexandria which, by 300 B.C., became a great intellectual center. A great museum was founded, and a library of 700,000 volumes was assembled, with the sciences allocated different floors in the library, in order of importance. Chemistry was relegated to the basement.

With the subsequent rise of the great Roman Empire, applied science was again in ascendancy. The Roman was not a philosopher, and did not contribute to pure science. Instead, he organized the science passed on to him from Greece. Sanitation was a feature of Roman life. Singer writes that

> "the finest monument to the Roman care of the public health stands yet for all to see in the remains of the fourteen great aqueducts which supplied the city with 300,000,000 gallons of potable water daily. No modern city is better equipped in this regard. . . . The distribution of water to individual houses was also well cared for, and excellent specimens of Roman plumbing may be seen in the British Museum."

Other industrial arts also flourished in ancient Rome. Color pigments discovered at Pompeii and Herculaneum were liberally applied in the decoration of buildings. The colors used were largely earth colors, such as yellow ochers, the red oxide of iron, naturally occurring vermillion, and copper-bearing minerals. Pompeian red, for example, is famous.

**6. Alchemy through the Middle Ages.**—In addition to applied chemistry and pure chemistry, another industry flourished in the Mediterranean countries even before the Christian era. It may be termed the art of *imitation*. Thus, imitation pearls were produced from secretions found in bamboo; and an excellent imitation of royal or Tyrian purple (which was obtained from a snail-like shell-fish of the Mediterranean, and was very expensive) was secured from plants. Not the least important of these imitations was the production of certain alloys which resembled silver and gold. Very beautiful and decorative color effects upon the surface of these alloys were achieved by heat treatment. Meanwhile, the Greek philosophers with their concept of the four elements of matter were led to believe that all metals were essentially alike, and capable of infinite change, one into the other. Metals were supposed to possess different degrees of purity, and it was believed that by subjecting them to fire and other agencies it was possible to pass step by step from the base metals to the noble metals—silver and gold. From this the imaginary art of transmuting lead into silver and gold was born, and since silver occurs together with lead in nature in the important ore *galena*, it is not so strange that the ancient chemist sometimes believed he had achieved success in transmuting a specimen of lead ore into silver. Our earliest record of transmutation, the Thebes papyrus of the third century A.D., contains a number of recipes written by members of the Greek colony at Alexandria for the production of alloys resembling gold to be used in the manufacture of imitation jewelry. By 290 A.D. Diocletian made inquiry

> "for all the ancient books which treated of the admirable art of making gold and silver, and without pity committed them to the flames, apprehensive as we are assured, lest the opulence of the Egyptians should inspire them with confidence against the empire."

By the middle of the seventh century the Arabs overran Egypt, becoming adept in the science of chemistry and infected with the lust for making gold. To the word *chemia* they added the Arabic article *al*, hence the word *alchemy*, fore-runner of modern chemistry. The Arabs spread alchemy over Spain and thence over western Europe. The darkness of the Middle Ages which followed, bred hope, suspicion and avarice in the heart of the chemist of those times. We can picture him feverishly spending his days in a vain search for gold. Let Paracelsus, a Middle Age contemporary, describe him.

> "An alchemist's laboratory is a gloomy, dimly lighted place full of strange vessels and furnaces, melting pots, spheres and portions of skeletons hanging from the ceiling, the floor littered with stone bottles, alembics, great parchments, books covered with hieroglyphics, the bellows with its motto 'spira spera'—breathe and hope—the hour glass, the astrolabe, and over all cobwebs, dust, and ashes. The walls are covered with various aphorisms of the brotherhood, legends and memorials in many tongues."

By the fourteenth century, frauds and quacks had multiplied so rapidly throughout western Europe that the Margrave of Beyreuth constructed a special gallows for the hanging of chemists, upon which was engraved

> "I once knew how to 'fix' (transmute) mercury, but now I am myself fixed."

But alchemy was more than a vain thirst for silver and gold; in its broader meaning it stood for the chemistry of the Middle Ages. For in addition to the fraud there was a second type of alchemist: the erratic philosopher. He it was who pursued the "philosopher's stone," the "elixir of life," which was believed by such eminent men as Roger Bacon to possess the power of prolonging life and of healing disease. The Bacons, Roger and Francis, who lived during the thirteenth and fifteenth centuries respectively, were staunch advocates of the experimental method in science. Ofttimes these alchemists were mystics, well illustrated by a recipe published by one of them for preparing a bit of the philosopher's stone.

> "You will separate the earth from the fire, the subtle from the compact, gently, with great skill. It ascends from earth to heaven, then descends again to earth, and receives the force of those above and those below. . . . This is the strong strength of all strength, because it will overcome every subtle thing, and penetrate every solid."

**7. The Iatrochemical Period.**—In the sixteenth century, chemistry strove to free itself from the domination of the alchemistic idea, and the era of Medical Chemistry, or the Iatrochemical (Greek *ιατρός, physician*) period, began. Chemistry was regarded as the handmaid of medicine, and many valuable medicines were discovered. The great precursor of the Medical Chemists was the renowned Paracelsus, who was born in Switzerland in 1493, and was the son of a physician. He gave a new direction to alchemy, declaring that

> "the object of chemistry is not to make gold but to prepare medicines";

and this union of chemistry with medicine was a dominant characteristic of the Iatrochemical School.

Paracelsus declared that the human body consists of sulfur, mercury, and common salt, and that the health of the body depends upon the presence of the proper amounts of these substances; when any of these ingredients is changed, illness results, and it can be cured only by the administration of chemical medicines. Familiar with the works of magicians and alchemists, he travelled long distances on foot, collecting a variety of information regarding the art of healing, from wise men and women, barbers, blacksmiths and others. He also spent much time in the mines of the Tyrol. After many strange experiences and vicissitudes this remarkable man again resumed his wanderings, and was finally thrown from a window and killed by the servants of a physician in Salzburg, in 1541.

Paracelsus contributed to medicine many valuable preparations, such as tincture of opium, or laudanum—the name by which it is still known. He was a close observer, and his practice of medicine was based upon careful observation now universally recognized. He used to say that all the accumulations of the medical lore before him were not worth the sole of his boot. His motto was:

> "Let him not belong to another who may be his own."

Other renowned men of the Iatrochemical period were Georg Agricola, J. B. Van Helmont, and J. R. Glauber. Of these, Agricola was born in Germany in 1490, and he became a noted physician. He was therefore a contemporary of Paracelsus, but, unlike the latter, he was not much interested in the storms which raged in the field of medicine at that time. Agricola pioneered in metallurgy, or the art of extracting metals from their ores. He was led to devote himself to mineralogy and metallurgy by the flourishing mining and smelting industry of Saxony. His great work on winning metals from their ores, *De Re Metallica*, served as a useful text-book until comparatively recent times; and was translated in 1912 by the Honorable and Mrs. Herbert Hoover.

**8. The Period of the Phlogiston Theory, from Boyle to Lavoisier.**—The era of medical chemistry continued up to the end of the seventeenth century, when certain views entertained by Paracelsus and others were overthrown by Robert Boyle (1626–1691), a far-seeing philosopher, who was the first real chemist in the scientific sense of the term. Boyle is best known as the author of *The Sceptical Chymist* and as the discoverer of the law which is associated with his name. He was a contemporary of Newton. Boyle, following the method of Roger Bacon, laid great stress on experimental and inductive methods.

> "First to doubt, then to enquire, and then to discover,"

was his method. He also clearly defined an "element" for the first time.

About this time Becher and Stahl of Germany advanced the Phlogiston Theory to explain the nature of fire or combustion. Plato had assumed that all combustible bodies or substances contained a common element—inflammable principle—which enabled them to burn. This explanation of combustion had been quite generally accepted. Some scholars thought that the inflammable principle was sulfur; hence the saying, "Where there are fire and heat, there is sulfur." But in 1669, Johann Becher pointed out that there are many combustible materials which do not contain sulfur; and he postulated in its place a principle termed by him *terra pinguis*, meaning fatty or inflammable earth. Subsequently Georg Ernst Stahl, who was a professor at Halle and a good chemist and successful teacher, developed Becher's hypothesis and gave the name **phlogiston** (Greek *φλογιστός, set on fire*) to his *terra pinguis*. Stahl and his followers held that when bodies burned or when metals were calcined, a sort of fire-stuff (*phlogiston*) escaped. Nobody seemed to have a very definite notion as to the real nature of phlogiston. Some thought that sulfur and soot were nearly pure phlogiston; others, that phlogiston was immaterial, or light, or hydrogen; and it was not uncommon for the same person to waver between these different opinions. For a hundred years this erroneous concept held sway, and influenced the interpretation of chemical phenomena.

9. **The Dawn of Modern Chemistry.**—On August 1, 1774 Joseph Priestley made a discovery which led to the overthrow of the phlogiston theory, and the dawn of our modern era in chemistry. Improved methods for the collecting and handling of gases had been devised, and their properties excited the curiosity of the scientific world. And then came Priestley's preparation of a new gas, oxygen; and it was soon proved by Lavoisier that oxygen, not phlogiston, was involved during combustion; that a substance burned in the air by uniting with oxygen. The old phlogiston theory was quickly abandoned, and our modern age of chemistry was ushered in.

From this time on, science became chiefly experimental, and the physical properties of substances were studied intensively. Henry Cavendish established that hydrogen was an element, and that hydrogen burned with oxygen to form water; Karl Scheele prepared chlorine and other gases. The **chemical balance** became an important instrument when Lavoisier demonstrated the supreme significance of the relative weights of reacting substances during chemical changes. These relative weights were soon associated with the weights of tiny particles called **atoms,** which John Dalton (1766–1844) had postulated. This atomic concept became the basis of modern theoretical chemistry. Meanwhile the great Swedish chemist, J. J. Berzelius, had prepared tables of the relative weights of these atoms, and chemical symbols to represent them.

By the middle of the nineteenth century the chemistry of living matter had become a fact. It is called **organic chemistry,** and studies the chemistry of compounds containing carbon. Then followed the rise of **physical chemistry,** relating the physical properties of atoms to their chemical behavior. By the end of the century radioactivity had been discovered, and chemists were peering inside the atom.

The first two decades of the twentieth century found an amazing extension of our knowledge of what goes on within the atom. Shortly a new type of mathematics, wave mechanics, was to become the tool of the chemist in predicting the behavior of matter. Shortly the atom was to be smashed and a thousand transmutations such as the alchemist dreamed of were to be achieved. Shortly the organic chemist was to synthesize complicated molecules in the laboratory.

Meanwhile pure chemistry became the handmaiden of industry. By 1930 technical laboratories had set up their own pure research laboratories. The wonderful Aladdin's lamp of industry was about to be rubbed. Textiles from coal, rubber from limestone and petroleum, sugar from sawdust, explosives and fertilizers from the air—these were a few of the offspring of the marriage between pure research and applied chemistry.

And it is our task, in the pages which follow, to trace the experimental research which has made them all possible.

## QUESTION REVIEW

### I. INTRODUCTION.

**a. Chemical Industry (1)**

NOTE: numbers in parentheses correspond to sections.

1. Name three modern synthetic products and the raw materials from which they are fashioned.

**b. Chemistry in other sciences (2).**

2. Describe some role played by chemistry in (*a*) astronomy, (*b*) physics, (*c*) geology, (*d*) biology.

**c. Pure chemistry (3).**

3. What is the aim of pure research?
4. Try to answer one of the questions raised in section 3.
5. In what way is a pure research worker unique?
6. How does research today differ from research in ancient times?
7. Approximately when did the experimental method begin to flourish?

### II. HISTORY OF CHEMISTRY.

**a. Applied chemistry in Egypt (4).**

8. Account for the name "chemistry."
9. List 5 applied arts practiced by the Egyptians.
10. What role did medicine play in early Egypt?
11. What other great peoples had a chemical industry?

**b. Chemistry in ancient Greece and Rome (5).**

12. Why did pure chemistry originate in Greece while applied chemistry progressed in Egypt?
13. Describe the composition of matter according to the doctrine of Empedocles and Aristotle.
14. What is meant by the "quintessence of beauty"?
15. What specifically did Aristotle do which won for him a distinction in the scientific world?
16. How do you know that pure chemistry was not held in high regard in Alexandria?
17. Analyze the relative importance of pure and industrial chemistry in Rome.

**c. Alchemy through the Middle Ages (6).**

18. Why might an ancient believe he had accomplished the transmutation of lead into silver?
19. How did transmutation accord with Empedocles' doctrine?
20. Mention one ancient record of alchemy.

21. Account for the name "alchemy."
22. Describe two sorts of alchemists of the Middle Ages.

**d. The Iatrochemical period (7).**

23. Describe the accomplishments of Paracelsus.
24. Describe the accomplishments of a contemporary of Paracelsus. Was the latter a pure chemist or an industrial chemist?

**e. The Phlogiston period (8).**

25. Why is Boyle considered a modern scientist?
26. How did Plato explain combustion?
27. What difficulty did Becher find with Plato's explanation?
28. Describe the theory of Becher and Stahl. What evidence have you that their theory must have been important?

**f. The dawn of modern chemistry (9).**

29. What discovery overthrew the Phlogiston theory? Explain why.
30. What were chemists interested in at the time of the American Revolution?
31. Name two important contributions of Lavoisier.
32. Identify an accomplishment each of Black, Cavendish, Priestley, Dalton, and Berzelius.
33. What branch of chemistry expanded rapidly during the middle of the nineteenth century? Shortly thereafter? At the close of the century?
34. What great achievements have been realized in pure chemistry in this twentieth century?

**Reading References:** Articles number 13, 15, 59, 205, 326, 403, 408 listed in the bibliography on pages 751–765. Number 205, for instance, refers to the article on "The American Spirit in Chemistry" by E. F. Smith in the Journal of Industrial and Engineering Chemistry, volume 11, pages 405 to 410, for the year 1919.

# CHAPTER II

# ELEMENTS AND COMPOUNDS. ATOMS AND MOLECULES. SYMBOLS AND FORMULAS

**10. Elements.**—Water is not a simple substance. It is composed of two colorless gases, oxygen and hydrogen. Oxygen is in the air which we breathe, and keeps us alive. If it were not there, life on earth would cease. Hydrogen is the gas used to fill rubber balloons; and since hydrogen is the lightest gas known, toy balloons tug at their strings.

### DEMONSTRATION 1. FORMATION OF WATER FROM ELEMENTS. RUSTING

Materials: Narrow neck bottle wrapped in heavy wire and filled with equal volumes of hydrogen and oxygen, splinter, burner, bright iron nail, rusty iron nail.

Now if we take a bottle containing a mixture of oxygen and hydrogen and apply a burning splint to it, a violent explosion occurs; the gases disappear, and in their place we find a thimbleful of water. In chemical language we say that the two **elements,** oxygen and hydrogen, have combined to form the **compound,** water. Again, when iron rusts, the element iron chemically combines with the element oxygen to form the compound, iron oxide. By certain devices the chemist can separate water into hydrogen and oxygen, or iron oxide into iron and oxygen. But by no simple means can oxygen, or hydrogen, or iron be further decomposed. These three simple substances are called **elements.** Chemists now have reason to believe that there are only 92 elements on this earth, of which 90 had been positively identified by 1941. All the compound substances known to us have been formed by the combination, or chemical union, of these elements. Microscopic traces of elements number 93, 94 and 95 were produced in the laboratory by McMillan and Abelson in 1940, confirming previous work by Fermi. Presumably they are quite unstable and break down into one of the well-known 92 elements. Their existence is of academic interest only.

Robert Boyle, in 1661, was the first scientist clearly to define an element. According to him, "the elements are the practical limits of chemical analysis, or are substances incapable of decomposition by any means with which we are at present acquainted."

While the definition of an element given by Boyle answers for practical purposes at the present time, the student should know that certain substances which were once regarded as elements have since been decomposed into simpler substances. Thus, Humphry Davy, early in the nineteenth century, succeeded in the isolation of such metals as calcium, sodium, and potassium from hitherto undecomposed substances which were regarded as elements. Quicklime, *e.g.*, was regarded as an element until Davy (1807) showed it to be an oxide of calcium.

In recent years scientists have discovered that certain substances known as **radioactive elements** decompose spontaneously into other elements. Thus, the element radium spontaneously splits up, yielding a number of other elements, such as helium, radon, and lead. Also, since 1919 these transmutations have been achieved artificially in the laboratory, lately by the aid of powerful electrical machines, such as the cyclotron. For convenience, however, the concept of "element" is still retained today, with the understanding that unusual treatment may result in its decomposition into other elements or particles.

**11. Metals and Non-metals.**—The elements have long been classed as metals, and as non-metals. This classification is not ideal, for certain elements do not fall sharply into either class, *i.e.*, they possess both metallic and non-metallic characteristics.

Metals and non-metals do have certain physical differences however. Metals, *e.g.*, silver and gold, show what is known as a metallic luster; they are malleable, ductile, and are good conductors of electricity.

On the other hand the non-metals, in general, do not possess these characteristics. Metals, as a rule, have greater densities and higher melting points and boiling points than do the non-metals.

The reader is undoubtedly familiar with a few of these elements. Sodium and chlorine combine to form common table salt, sodium chloride; calcium and oxygen form quicklime; magnesium is the shiny metal used for photographic flashlight bulbs; we find aluminum foil in another type of photoflash bulb, aluminum in our kitchens, aluminum for structural purposes in auto, building or bridge. These **light metals** were not known to the ancients since they can only be liberated from their compounds with difficulty.

The **heavy metals**, gold, silver, copper, tin, lead, mercury and iron, on the other hand, were well known owing to the fact that they occur free in nature (*e.g.*, native gold) or can be readily prepared from certain of their ores. Zinc did not come into general use until comparatively recent times. Mercury is our only metal which is liquid at ordinary room temperatures, although there are two other metals, caesium and gallium, which will melt on a really hot day (M.P. 26.4° C. and 30° C. respectively). The metals in the third column of Table 2 are added to iron to make special steels.

Bronze is not an element for it is made of copper and tin; neither is brass, which contains copper and zinc.

The **non-metals** are less familiar to the layman than the metals. Chlorine was the first deadly war gas used in large quantities; bromine is a vile-smelling liquid; iodine is a dark-gray solid, familiar to us as "tincture of iodine" which is a solution containing approximately 7 grams of iodine and 5 grams of potassium iodide in 100 cubic centimeters of alcohol. Helium is used for balloons; and from the air we extract neon for signs and argon for our electric light bulbs. Oxygen and nitrogen we inhale. Our grandparents who took sulfur and molasses, or used sulfur candles for fumigation, or struck phosphorus matches before the days of the safety match are more familiar than we with these two elements. Arsenic compounds are used in fumigants; our lead-pencil is made of carbon and clay, not of lead; and sea-sand is a compound containing the elements oxygen and silicon.

The classification of some of the more familiar elements follows.

TABLE 1. LIGHT METALS (DENSITY LESS THAN 5)

| **Alkali metals** | **Alkaline earth metals** | |
|---|---|---|
| sodium | calcium | magnesium |
| potassium | barium | aluminum |

TABLE 2. HEAVY METALS (DENSITY BETWEEN 5 AND 22)

| **Noble metals** | **Base metals** | **In special steels** | |
|---|---|---|---|
| gold | copper | nickel | zinc |
| platinum | lead | manganese | |
| silver | mercury | cobalt | |
| | iron | tungsten | |
| | tin | chromium | |

TABLE 3. NON-METALS (GROUPED IN FAMILIES)

| **Halogens** | **Inert gases in air** | | | |
|---|---|---|---|---|
| fluorine | helium | oxygen | nitrogen | carbon |
| chlorine | neon | sulfur | phosphorus | silicon |
| bromine | argon | | arsenic | |
| iodine | | | | |

You will notice that these non-metals have been arranged in families; which, as we shall learn in more detail later, is a convenient way for the chemist to group different elements which have strikingly similar properties.

DEMONSTRATION 2. METALS AND NON-METALS

Materials: Table salt, sodium, chlorine, quicklime, magnesium ribbon, photoflash bulb, gold, silver, copper, mercury, bromine, iodine, tincture of iodine, sulfur, phosphorus, graphite, silicon.

**12. Chemical Composition of Some Familiar Bodies.**—F. W. Clarke has made an estimate of the occurrence of the elements in the solid shell of the earth, in the sea and other waters, and in the air.

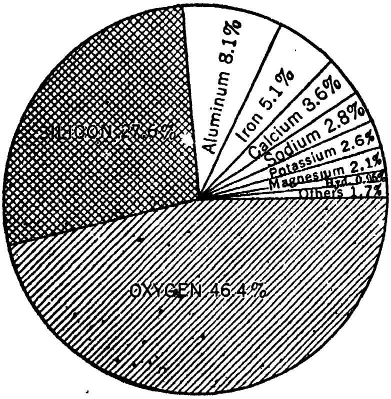

FIG. 2. Composition of the earth's crust. Shaded portion non-metals. White portion metals.

An examination of Clarke's table shows that **twenty elements constitute 99.7 per cent of the earth's crust.** The other seventy-two elements are estimated to constitute 0.33 per cent (Fig. 2).

The **sun** contains essentially the same metals as the earth. Thus in both bodies iron and nickel are a hundred times more abundant than copper and zinc. Some elements are usually rare in both: lithium, beryllium, scandium, gallium and indium. On the other hand elements present in the earth's atmosphere are vastly more abundant in the sun's atmosphere. Thus carbon dioxide is nearly a hundred times, nitrogen ten thousand times, and helium ten million times more abundant on the sun than on the earth. This forces us to the conclusion that the earth has lost a

TABLE 4. COMPOSITION OF THE EARTH'S SHELL. F. W. CLARKE AND WASHINGTON

| | Solid Shell 93 Per cent | Ocean 7 Per cent |
|---|---|---|
| Oxygen | 46.4 | 85.79 |
| Silicon | 27.6 | .... |
| Aluminum | 8.1 | .... |
| Iron | 5.1 | .... |
| Calcium | 3.6 | 0.05 |
| Sodium | 2.8 | 1.14 |
| Potassium | 2.6 | 0.04 |
| Magnesium | 2.1 | 0.14 |
| Hydrogen | 0.13 | 10.67 |
| Titanium | 0.46 | .... |
| Carbon | 0.19 | 0.002 |
| Chlorine | 0.07 | 2.07 |
| Bromine | .... | 0.008 |
| Phosphorus | 0.12 | .... |
| Sulfur | 0.12 | 0.09 |
| Barium | 0.08 | .... |
| Manganese | 0.08 | .... |
| Strontium | 0.02 | .... |
| Nitrogen | .... | .... |
| Fluorine | 0.10 | .... |
| Other elements | 0.33 | .... |
| | 100.00 | 100.00 |

great deal of its atmosphere, whereas the sun has not. There is 300 times more hydrogen in the sun's atmosphere than all the metals put together. Non-metals were not discovered in the sun until 1934, but oxygen, nitrogen, sulfur and phosphorus have since been confirmed by Babcock and Moore. Ozone in the earth's atmosphere makes it impossible to identify the presence of the halogens, the inert gases, gold, mercury, and caesium. In the sunspots, which are cooler, lithium, rubidium and boron in the form of boron oxide are detected. Neither bismuth nor radium has been discovered there. **Venus** has an atmosphere of carbon dioxide, practically no water, and if there is any oxygen there it must be less than one thousandth of the quantity in our own atmosphere. Our **Moon** is not heavy enough to hold the lighter gases such as oxygen, nitrogen, or water upon its surface; although carbon dioxide could be present. **Mars** probably has an ice-cap. **Saturn** has a density of 0.26; and since all liquefied gases excepting helium and hydrogen have densities greater than that, it is assumed that the 20,000 miles of atmosphere above that planet consists of those two elements. The **asteroids** have no atmosphere at all, since their gravitational pull is not sufficient to hold gases to their surfaces. The **comets** are similar to the sun in composition, although they may be cold enough to freeze all but hydrogen and helium; or hot enough, when they are near the sun, to melt platinum. Of the **meteorites** which fall upon our earth, 97 per cent of them consist of silicon compounds, while only 3 per cent of them are of iron, contrary to popular opinion. No new elements have ever been found in meteorites.

When the materials in the **human body** are analyzed only a limited number of the elements are found to be present (Fig. 3). Nearly the whole of the bulk of the fluids and softer portions of the body are made up of the four nonmetals: oxygen (64%), carbon (20%), hydrogen (10%), and nitrogen (2%). The bones contain compounds of calcium (2%) and phosphorus (1.1%). There is also about 0.1 per cent each of sulfur, potassium, sodium and magnesium. A few other elements are present only in traces, and yet they are apparently vital to the life-processes of man. These elements are iron, iodine, chlorine, fluorine, lithium, arsenic, silicon and manganese.

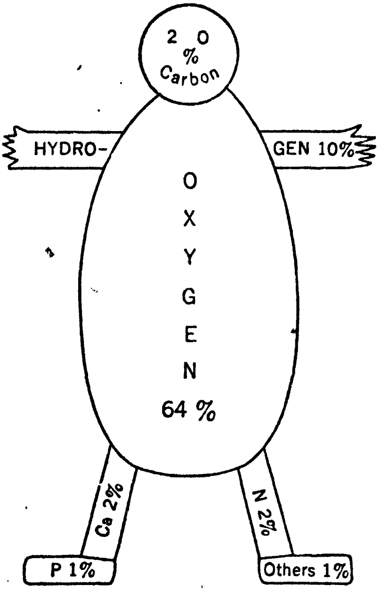

FIG. 3. Approximate composition of the human body.

**13. Compounds.**—Thus far we have considered the 92 different elements as building blocks of matter. As intimated in section 10, these elements combine to form compounds. Thus oxygen and hydrogen unite to form water; iron and oxygen form iron oxide. These are but two of the half a million known compounds, of which over 300,000 contain no elements other than carbon, hydrogen, oxygen and nitrogen.

Now it is an astonishing fact that the properties of any given compound are unique for that compound. No known substance other than water possesses the properties described below; and therefore when we examine a sample of some unknown liquid and find it has these properties, we can confidently conclude it is water. These properties are: it is odorless, tasteless, colorless when viewed in thin layers; it boils at 100° C. and freezes at 0° C., under atmospheric pressure; it leaves no residue when evaporated to dryness.

Another important fact about compounds concerns the quantities of elements in them. For example, repeated analysis of water will reveal that every 100 grams of water always contains 11.19 grams of hydrogen and 88.81 grams of oxygen. In the same way, carbon and oxygen form a compound, carbon monoxide, where the percentages, by weight, of its constituents are always 42.9 per cent carbon and 57.1 per cent oxygen. This fact has been generalized into a law which states that **any given compound always contains the same elements in chemical union, and they are always present in a constant proportion by weight.** This law, one of the many generalizations which the chemist has made about matter, is known as the **Law of Definite Proportions.**

**14. Mixtures.**—The Law of Definite Proportions does not apply to mixtures, for the components of a mixture may be mingled in practically any proportion. Thus hydrogen and oxygen may be mixed in any ratio at room temperature without explosion occurring; and it is not until heat is applied that a chemical reaction occurs, resulting in the formation of the compound, water. Whatever portion of hydrogen or of oxygen is in excess of the 11.19 : 88.81 ratio will remain unchanged after the explosion has occurred.

In general the constituents [1] of a chemical compound can only be liberated by chemical change, since the chemical bonds uniting them must be broken; whereas the components of a mixture can usually be rather easily separated by physical means.

Ordinary concrete is a mixture of crushed stone, sand, and cement; gunpowder, a mixture of potassium nitrate (saltpeter or niter), sulfur, and charcoal.

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[1] Note that the word *components* refers to the parts of a mixture; but the word *constituents* is reserved for the parts of a compound.

## ATOMS AND MOLECULES

**15. The Atomic Theory.**—The structure of matter engaged the attention of philosophers of the East long before the days of Grecian philosophy. Kanada, the founder of a system of Hindu philosophy, taught that matter was made up of exceedingly small, indivisible, eternal particles called **atoms** (Greek, meaning *uncut, indivisible*), which were supposed to be in perpetual motion and separated from one another by void space.

The ancient Greek philosophers were divided into two schools. On the one hand there was the school of Aristotle (384–322 B.C.), called the Peripatetic, because the pupils received instruction while walking in the Lyceum at Athens. They taught that matter is infinitely divisible. On the other hand, the school of Atomistic philosophers, led by Democritus, held that matter is finitely divisible—*i.e.*, composed of atoms. Democritus (470–360 B.C.) taught that atoms of different sizes and forms float about in the void and impinge on one another, the atoms of similar form tending to group themselves together. The theory of the Atomistic philosophers contained the germ of the modern theory of the structure of matter.

Sir Isaac Newton (1642–1727) had the idea that matter was formed in solid, hard, impenetrable, movable particles; and that these primitive particles are incomparably harder than any porous bodies compounded of them.

The speculation of ancient philosophers was virtually all that was known about the structure of matter until the beginning of the nineteenth century, when John Dalton (1766–1844), a schoolmaster of Manchester, England, quickened the dead dogma of the early speculators into a living hypothesis. The essence of Dalton's atomic theory, which was formulated at the very beginning of the nineteenth century (about 1803), may be stated as follows:

(1) *Every element is made up of exceedingly small, indivisible, indestructible particles called atoms.*

(2) *The atoms of different elements possess different weights, but those of a particular element are constant in weight.*[1]

(3) *Chemical compounds are formed by the union of a definite whole number of atoms of the constituent elements.*

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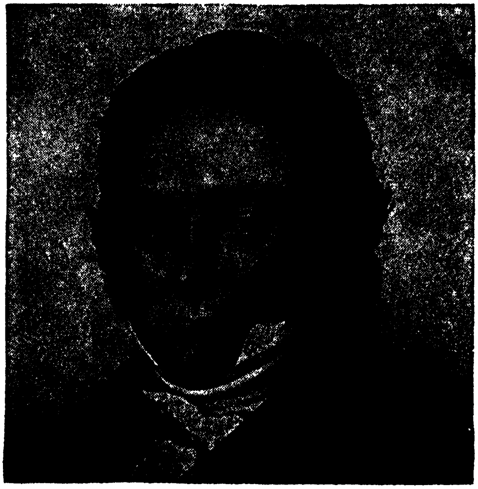
[1] This statement must be somewhat qualified in the light of recent discoveries of *isotopes*, page 155, but will serve as a satisfactory working basis.

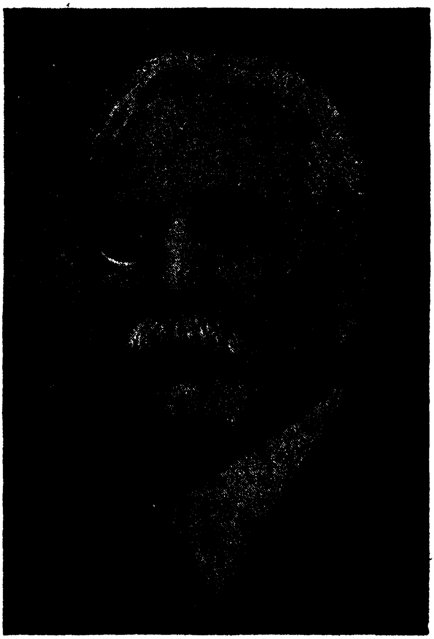


JONS JAKOB BERZELIUS
(1779–1848)

Professor of medicine and pharmacy at Stockholm (1807–32); author of the system of chemical symbols still in use (1811); a remarkable analyst who prepared a table of accurate atomic weights (1826); discovered Se, Th, Si, and first isolated Zr; propounded his celebrated electro-chemical theory according to which every compound consists of two parts, one positive, the other negative.

THEODORE WILLIAM RICHARDS
(1868–1928)

The first Nobel Laureate in Chemistry from the United States (1914); Professor of Chemistry at Harvard University; noted for his work in physical chemistry, especially his accurate determinations of atomic weights, atomic volumes, and electro- and thermochemical properties. His son-in-law, James Bryant Conant, an organic chemist of considerable repute, is now (1941) President of Harvard University.



**16. Relative Weights of Atoms.**—According to one of the postulates of Dalton, atoms of different elements possess different weights. Though individual atoms are far too small to be seen or weighed, we have indirect methods for determining their exact weights, as will be described in a subsequent chapter. Thus an atom of gold weighs 0.000 000 000 000 000 000 000 3254 grams. The awkwardness of handling such a number is at once apparent, so the chemist employs a system of *relative weights, taking oxygen as the standard, weight 16.0000.* The atomic weights of the other elements are expressed in terms of this. Thus, the sulfur atom is approximately twice as heavy as the atom of oxygen, so its atomic weight is 32. The atomic weights of a few of the common elements follow.

TABLE 5. ATOMIC WEIGHTS OF SOME ELEMENTS

| ELEMENT | INTERNATIONAL ATOMIC WEIGHTS (1940) |
|---|---|
| **Oxygen** | **16.0000** |
| Hydrogen | 1.0080 |
| Carbon | 12.010 |
| Nitrogen | 14.008 |
| Calcium | 40.08 |
| Silver | 107.880 |
| Gold | 197.2 |
| Lead | 207.21 |
| Uranium | 238.07 |

The hydrogen atom is the lightest (approximately 1), and the atom of uranium is the heaviest—nearly 15 times as heavy as the oxygen atom.

**17. The Atomic Theory Explains the Law of Definite Proportions.**—The particles formed by the union of atoms are called **molecules** (Latin, *a little mass*). Thus one *atom* of carbon combines with one *atom* of oxygen to form one *molecule* of carbon monoxide. In the case of water, it is found that two atoms of hydrogen combine with one atom of oxygen to form one molecule of water. With this picture of atoms and molecules, the law of definite proportions is an immediate consequence. For if every molecule of carbon monoxide, for example, contains one atom of carbon, weighing 12.010 units, and one atom of oxygen, weighing 16.0000 units, the resulting molecule of carbon monoxide will weigh $12.010 + 16.0000 = 28.010$ units, and the relative proportions of carbon and oxygen in this molecule will be 12.010/28.010 and 16.0000/28.010 or 42.9 per cent and 57.1 per cent respectively.

Dalton's original atomic theory has been somewhat modified. The term *molecule* was not used by Dalton, but was introduced by the Italian physicist, Avogadro, in 1811.

The atomic theory appears to rest upon a firm foundation despite the fact that it has been necessary to modify it somewhat on account of the discovery of new facts, such as radioactivity and isotopes. There is much independent proof that atoms and molecules really exist, and chemists even know something about the structure of atoms.

## SYMBOLS, FORMULAS, NOMENCLATURE

**18. Names and Symbols of the Elements.**—A great many of the elements have been given names derived from the Greek: *e.g., hydrogen* (*water-producer*); *chlorine* (*yellowish-green*); *iodine* (*like a violet*—from its violet vapor); *helium* (*the sun*—for it was first discovered in the sun). Others originate from the Latin, *e.g., tellurium* from Latin *tellus*, the earth; *copper* from Latin *cuprum*, the Island of Cyprus where it was mined in quantity. Still other elements are named after particular localities, *e.g., strontium* from Strontian in Scotland; *germanium*, discovered in Germany; and *scandium*, in Scandinavia.

Since the constant use of these full names of the elements would be cumbersome, the chemist soon developed a chemical shorthand for representing them. These are called the **chemical symbols.**

The crude symbols used by the alchemist of the Middle Ages were as awkward as the full names. Thus, gold was represented by the symbol ☉ or 🌞, for the sun; silver, by ☾, the moon. The symbol △ was used by Lavoisier for water. Dalton represented the atoms of elements by symbols, which he combined to represent the elements in a particular compound: *e.g.*, ☉ stood for hydrogen; ○, for oxygen. Water was represented by ☉ ○.

In 1811, J. J. Berzelius, the great Swedish chemist, revolutionized chemical shorthand by introducing a simplified system of symbols. His system, which is in use today, was to use one or two letters of the name of the element—often from the Latin or the Greek name. Thus **Au** indicates the element gold or *aurum*, **Fe** represents iron or *ferrum*, **Hg** represents mercury or *hydrargyrum*, "water silver." The merit of the Berzelius system is that it is international, so that American, German, Frenchman, Englishman, Italian, Occidental or Oriental, all speak a common chemical language.

In the table below are listed a few of the symbols which should be memorized for immediate use in this course. All 92 symbols will be found in the chart on the inside of the back cover of this book.

TABLE 6. SYMBOLS OF COMMON ELEMENTS

| ELEMENT (metals) | SYMBOL ↓ | ELEMENT (non-metals) | SYMBOL ↓ |
|---|---|---|---|
| Aluminum | Al | Bromine | Br |
| Barium | Ba | Carbon | C |
| Calcium | Ca | Chlorine | Cl |
| Copper (cuprum) | Cu | Iodine | I |
| Gold (aurum) | Au | Nitrogen | N |
| Iron (ferrum) | Fe | Oxygen | O |
| Lead (plumbum) | Pb | Phosphorus | P |
| Magnesium | Mg | Silicon | Si |
| Manganese | Mn | Sulfur | S |
| Mercury (hydrargyrum) | Hg | | |
| Potassium (kalium) | K | | |
| Silver (argentum) | Ag | | |
| Sodium (natrium) | Na | | |
| Zinc | Zn | | |

(Hydrogen H)

It will be noticed from table 6 that many metals, or their Latin roots, end in *um* or *ium*; while non-metals usually end in *ine*, or *on*, or *gen*.

The student should note the exact meaning of the symbols. O stands for 16 parts by weight, or one atom, of oxygen. H stands for 1.0080 parts by weight, or one atom, of hydrogen. C stands for 12.010 parts by weight, or one atom, of carbon. 3O stands for three atoms of oxygen, or 48 parts by weight.

As the symbols stand for parts by weight of the different elements, we can express the weights in grams, if we like, obtaining the atomic weight in grams, or the **gram-atomic weight.** Thus, the gram-atomic weight of oxygen is 16 g.

**19. Formulas.**—We have seen that elements combine to form compounds; also, that the particles formed by the union of atoms are called **molecules,** which are **clusters, or aggregates, of which the atoms are the units.** Chemists represent a molecule of a substance by a combination of symbols, which is known as a **chemical formula.** Thus magnesium and sulfur combine to form the product magnesium sulfide:

$$Mg + S \rightarrow MgS.$$

MgS stands for a molecule of magnesium sulfide, consisting of one atom of magnesium and one atom of sulfur.

A few formulas and their significance follow.

NaCl represents one molecule of sodium chloride;
$ZnCl_2$ represents one molecule of zinc chloride, which contains one atom of zinc and two atoms of chlorine;
$3H_2O$ represents three molecules of water, a total of 6 atoms of hydrogen and 3 atoms of oxygen.

Each formula represents not only a molecule but also a given weight of the substance. For the sum of the weights of the atoms in a molecule gives what is known as the **molecular weight** of the molecule. Thus, the molecular weight of water ($H_2O$) is equal to $(2 \times 1.0080) + 16 = 18.0160$. This means that 18.0160 parts by weight of water contain 2.0160 parts of hydrogen and 16 parts of oxygen: *e.g.*, 18.0160 g. of water when decomposed yield 2.0160 g. of hydrogen and 16 g. of oxygen.

The molecular weight of a substance, expressed in grams, is known as a **gram-molecular weight,** or **mole:** *e.g.*, the molecular weight of carbon dioxide ($CO_2$) is $12 + (2 \times 16) = 44$; hence 44 g. of carbon dioxide is a gram-molecular weight.

**20. Types of Compounds. Valence. Nomenclature.**—Not all atoms will combine with one another to form molecules. The most common types of molecules follow.

**a. Diatomic Gases, Monatomic Solids.** Of the non-metals in table 3 the following gases occur in the free state as double atoms, and are therefore written in the free state as diatomic molecules: $Cl_2$, $N_2$, $O_2$, and $H_2$. Bromine is a liquid and iodine a solid, but in the gaseous state they too are written as double atoms, *viz.* $Br_2$ and $I_2$. The metals and the inert gases are in general monatomic, *viz.* Na, K, Fe, He, A.

**b. Metal Plus Non-metal.** Any metal in tables 1 and 2 will combine with any non-metal in table 3 to form a compound. The name of the resulting molecule ends in *ide*, *e.g.*, CaO, calcium oxide; $AlCl_3$, aluminum chloride; NaCl, sodium chloride.

The reader will immediately be perplexed by his observation that there are three atoms of chlorine in aluminum chloride, but only one atom of chlorine in sodium chloride. The chemist has discovered an astonishing principle in nature which is usually followed in the formation of these molecules. Each element may

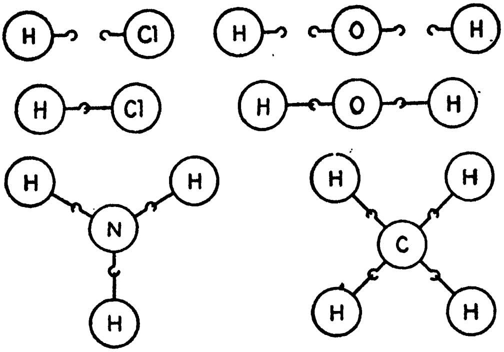


FIG. 4. Diagram representing valence by imaginary hooks.

be assigned a number, called **valence,** and no atoms will combine to form a molecule unless the sum of their valences is zero. For example, silver has a valence of + 1, and chlorine a valence of − 1. The molecule formed by the combination of these two elements must have the formula AgCl, since + 1 − 1 equals zero. $AgCl_2$ would be impossible since the sum of the valences would then be + 1 − 2 equals − 1. For the same reason the following formulas are correct, as a glance at the valences in table 7 will confirm: zinc chloride, $ZnCl_2$; magnesium sulfide, MgS; potassium nitride, $K_3N$; and aluminum oxide, $Al_2O_3$. The valences for these different elements are to be memorized later in the term.

TABLE 7. PRINCIPAL VALENCES OF SOME COMMON ELEMENTS

| | | | | |
|---|---|---|---|---|
| METALS | | | | |
| Constant Valence | $H^{+1}$ | $Na^{+1}$ | $K^{+1}$ | $Ag^{+1}$ |
| | $Mg^{+2}$ | $Ca^{+2}$ | $Ba^{+2}$ | $Zn^{+2}$ |
| | $Al^{+3}$ | | | |
| Variable Valence | | | | |
| $Cu^{+1}$ and $Cu^{+2}$ | | $Fe^{+2}$ and $Fe^{+3}$ | | $Mn^{+2}$ and $Mn^{+4}$ |
| $Hg^{+1}$ and $Hg^{+2}$ | | | | |
| NON-METALS | | | | |
| $O^{-2}$ | | | $Cl^{-1}$ and $Cl^{+3}$ and $Cl^{+5}$ | |
| $S^{-2}$ and $S^{+4}$ and $S^{+6}$ | | | $P^{-3}$ and $P^{+3}$ and $P^{+5}$ | |
| $C^{-4}$ and $C^{+4}$ | | | $N^{-3}$ and $N^{+3}$ and $N^{+5}$ | |
| | | | $I^{-1}$ | |

It will be noticed that some of the metals have two valences. Thus, it is necessary to distinguish between $FeCl_2$ and $FeCl_3$. They cannot both be called iron chloride. For such cases, the chemist suffixes the endings **ous** for the compounds in which the metal has the lower valence and **ic** for the compound in which the metal has the higher valence. Thus we call

$FeCl_2$ ferr**ous** chloride, and $FeCl_3$ ferr**ic** chloride;
HgBr mercur**ous** bromide, and $HgBr_2$ mercur**ic** bromide;
$Cu_2O$ cupr**ous** oxide, and CuO cupr**ic** oxide.

**c. Non-metal plus Non-metal.** Certain of the non-metallic atoms will combine with one another. Thus we have CO, carbon monoxide, and $CO_2$, carbon dioxide; $PCl_3$, phosphorus trichloride, and $PCl_5$, phosphorus pentachloride. It will be noticed that with this type of molecule when two different molecules are formed from the same elements, such as $PCl_3$ and $PCl_5$, they are distinguished by a prefix before the last element. These prefixes are as follows: for one atom *mono*, as in carbon **mono**xide, CO; for two atoms *di*, as in nitrogen **di**oxide, $NO_2$; three atoms *tri*, as in phosphorus **tri**oxide, $P_2O_3$; four atoms *tetra*, as in nitrogen **tetr**oxide, $N_2O_4$; five atoms *penta*, as in phosphorus **pent**oxide, $P_2O_5$. Note that the sum of all the valences in any one compound totals zero, *viz.* $P^{+3}Cl_3^{3(-1)}$; $P_2^{2(+5)}O_5^{5(-2)}$.

**d. Metal plus Non-metal plus Oxygen.** With this fourth type of molecule we shall, for a beginning, list only a few molecules for the student to remember; and all of these have names ending in **ate**. They are

(1) the **sulfates,** containing $(SO_4)^{-2}$ in compounds such as $ZnSO_4$, zinc sulfate; $CuSO_4$, cupric sulfate;
(2) the **nitrates,** containing $(NO_3)^{-1}$ in compounds such as $NaNO_3$, sodium nitrate; $AgNO_3$, silver nitrate; $Ca(NO_3)_2$, calcium nitrate;
(3) the **carbonates,** containing $(CO_3)^{-2}$ such as $CaCO_3$, calcium carbonate (limestones, pearls, coral); $Na_2CO_3$, sodium carbonate (washing soda);
(4) the **chlorates,** containing $(ClO_3)^{-1}$ such as $KClO_3$, potassium chlorate.

In all of these compounds, too, it will be observed that the sum of the valences in the molecule is zero. Thus for sodium carbonate we have

| | | | | |
|---|---|---|---|---|
| | $Na_2^{+1}$ | $C^{+4}$ | $O_3^{-2}$ | |
| Sum of valences | +2 | +4 | −6 | equals zero. |

## QUESTION REVIEW

### I. ELEMENTS AND COMPOUNDS.

**a. Elements (10).**

1. Describe in chemical terms (*a*) the formation of water, (*b*) the rusting of iron.
2. How many elements remain to be discovered? Locate them in the chart on the inside of the back cover of the book.
3. Why has Boyle's definition of an element been modified?

**b. Metals and non-metals (11).**

4. In what physical properties do metals in general differ from non-metals?
5. List 5 metals and 5 non-metals and mention one interesting fact about each.

**c. Chemical composition of some familiar bodies (12).**

6. List (*a*) the 5 most abundant elements in the earth's crust with approximate percentages, (*b*) the 6 most abundant elements in the human body, (*c*) elements in some heavenly bodies.

**d. Compounds (13).**

7. How would you distinguish between silver and platinum? Gold and brass? Wheat flour and starch? Common salt and calomel? Quartz and diamond?

**e. Mixtures (14).**

8. Which of the following are pure substances and which are mixtures: ice, muddy water, milk, copper, water, the atmosphere?
9. How would you separate ordinary gunpowder into its components? Sand and sugar? Alcohol and water?
10. Why is it incorrect to state that "the components of water are oxygen and hydrogen?"

### II. ATOMS AND MOLECULES.

**a. The atomic theory (15).**

11. Differentiate between (*a*) the Peripatetic and the Atomistic concept of matter, (*b*) the atoms of Dalton and of Democritus.

**b. Relative weights of atoms (16).**

12. What does it mean when we say that carbon has an atomic weight of 12.010? State the at. wt. of O. of H.

**c. The atomic theory explains the law of definite proportions (17).**

13. Explain the law of definite proportions in terms of the atomic theory.

III. SYMBOLS, FORMULAS, NOMENCLATURE.

**a. Names and symbols of the elements (18).**

14. Give the names of two elements with names derived from (*a*) the Latin, (*b*) the Greek, (*c*) localities.

**b. Formulas (19).**

15. For what do the following formulas stand: $H_2O$, $N_2O_3$, $N_2O_5$, $Hg_2O$, $HgO$, $KI$, $SO_2$, $SO_3$, $O_2$, $3Cl_2$, $2Cl$, $2O_2$?
16. Write the symbols for copper, gold, iron, lead, magnesium, manganese, mercury, phosphorus, potassium, silver, sodium and zinc.

**c. Types of compounds. Valence. Nomenclature (20).**

NOTE: At this early stage in the course the student is not expected to memorize valences. He should refer to table 7.

17. Describe the four most common types of molecules, giving an example of each.
18. Give the formula and name of a compound formed between a metal with variable valence and a non-metal.
19. Correct the following formulas: $AlCl_2$, $CaCl$, $Mg_2O$, $AgO$, $H_3O$, $M_2P_3$.
20. Write formulas for magnesium sulfide, mercuric nitrate, zinc sulfide, silver iodide, calcium oxide, mercurous oxide, mercuric oxide, magnesium sulfate.

**Reading References:** Articles number 7, 37, 39, 45, 59, 65, 66, 102, 210, 227, 403, 408, 423 in the Appendix.

# CHAPTER III

## CHANGES IN MATTER. WRITING OF EQUATIONS

### PHYSICAL CHANGES

**21. Physical Changes.**—In certain cases the changes about us are so slow as to be quite imperceptible day by day, while in other cases they are rapid. Many changes are **physical.** Familiar illustrations are: the magnetization and heating of iron, the conversion of trees into lumber, the crushing of stone, the formation of dew and frost. Water exists in three different states—the solid state (ice), the liquid state, and the gaseous state (water vapor, or steam). These states of water depend upon physical conditions—temperature and pressure. The inhabitant of the Arctic regions is very familiar with ice and snow, but to the inhabitant of the tropical regions this state of water is virtually unknown. Water vapor, which is always present in the atmosphere, frequently condenses to form clouds, rain, fog, and dew. The three familiar forms of water may be transformed into each other without gain or loss in weight and, from the viewpoint of the chemist, without any essential change in their nature.

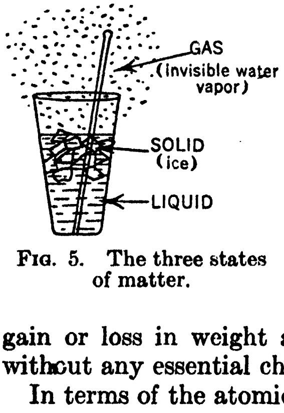


FIG. 5. The three states of matter.

In terms of the atomic theory, when a physical change occurs, the molecules preserve their integrity. Thus water remains essentially $H_2O$ throughout successive transformations into ice, steam and dew.

DEMONSTRATION 3. A PHYSICAL CHANGE

Materials: Test-tube containing a moth ball, beaker of water on tripod over burner.

When the moth ball is heated by placing the test-tube in boiling water, a colorless liquid is formed. The liquid solidifies into white crystals upon cooling. Explain.

### CHEMICAL CHANGES

**22. Chemical Changes. Writing of Equations.**—In many changes, however, the molecules are broken down and their parts unite to form new molecules. These are **chemical changes.** We are all familiar with the corrosion of metals, the combustion of fuel, the decay of animal and of vegetable matter, the souring of milk, the fermentation of sweet cider to form an alcoholic liquid, and the transformation of cider into vinegar.

The chemist has invented a chemical shorthand to express these chemical changes. Such a representation of a chemical reaction is called a **chemical equation.** The following examples will make the chemist's notation clear.

(1) When iron is heated with sulfur, ferrous sulfide is formed. The chemist writes:

$$Fe + S \rightarrow FeS.$$

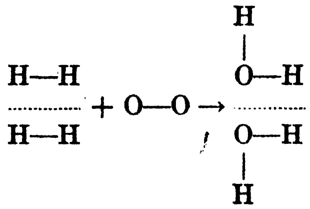
This equation reads: one atom of iron combines with one atom of sulfur to form one molecule of ferrous sulfide; or, iron combines with sulfur to give ferrous sulfide.

(2) When a mixture of hydrogen and oxygen gas is exploded, water is formed. The equation is:

$$2H_2 + O_2 \rightarrow 2H_2O \qquad \text{(correct equation).}$$

This equation reads: two molecules of hydrogen combine with one molecule of oxygen to give two molecules of water. A number of difficulties arise in balancing this equation. First, it would be incorrect to write $H_2 + O \rightarrow H_2O$, because we know that gaseous oxygen is present as the diatomic molecule, $O_2$ (section 20, a). Secondly, it would be incorrect to write $H_2 + O_2 \rightarrow H_2O_2$ because we know that the product which forms has the properties of water ($H_2O$) and not hydrogen peroxide ($H_2O_2$). Thirdly, it would be incorrect to write $H_2 + O_2 \rightarrow H_2O$ because no atoms were destroyed during the reaction; that is, the number of atoms on one side of the equation must equal the number on the other side. The correct equation above shows that at both the beginning and end of the reaction the number of atoms involved was 4 atoms of hydrogen and 2 atoms of oxygen.

A picture of what is happening amongst the atoms during the reaction would be



$$\begin{array}{c} \text{H—H} \\ \cdots\cdots \\ \text{H—H} \end{array} + \text{O—O} \rightarrow \begin{array}{c} \text{H} \\ | \\ \text{O—H} \\ \cdots\cdots \\ \text{O—H} \\ | \\ \text{H} \end{array}$$

(3) There is a technique in balancing equations just as there is a technique in solving cross-word puzzles. Let us illustrate by solving the following problem.

*Problem:* It is known that potassium chlorate, upon heating, breaks down into oxygen gas and potassium chloride. Write the equation for the reaction.

**Step a.** Write down the substances involved, making sure that the valences are properly balanced for the molecules concerned.

$$\begin{array}{lcccccc} & KClO_3 & \xrightarrow{\text{heat}} & KCl & + & O_2 & \text{(O is un-} \\ \text{Valences} = & [+1+5-6] & & [+1-1] & & [0] & \text{balanced).} \end{array}$$

Notice that oxygen must be written $O_2$, since gaseous oxygen is diatomic. The valence of a free element like this is zero.

**Step b.** Balance the number of atoms of each element. Thus we read

1K on the left, 1K on the right;
1Cl on the left, 1Cl on the right;
but 3O on the left, 2O on the right.

In order to make this oxygen balance we must write $2KClO_3$ and $3O_2$, *i.e.*,

$$2KClO_3 \xrightarrow{\text{heat}} KCl + 3O_2 \qquad \text{(K and Cl are unbalanced).}$$

It would be incorrect to write $KClO_3 \rightarrow KCl + 3O$; or $KClO_3 \rightarrow KClO + O_2$; or $KClO_3 \rightarrow KCl + O_3$, for these formulas do not represent the facts as stated in the original problem.

**Step c.** The equation is still unbalanced, for in changing the number of $KClO_3$ molecules we have unbalanced the K and Cl, since it now reads

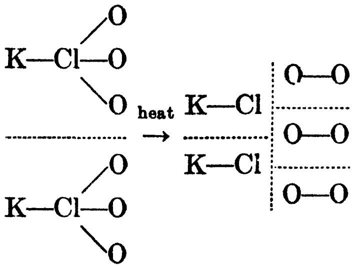
2K on the left; 1K on the right
2Cl on the left; 1Cl on the right
6O on the left; 6O on the right.

The obvious addition to be made is to increase the KCl on the right to 2KCl.

The completed equation then reads:

$$\mathbf{2KClO_3 \xrightarrow{\text{heat}} 2KCl + 3O_2 \uparrow} \qquad \textbf{(correctly balanced equation).}$$

which signifies to the chemist that 2 molecules of potassium chlorate will decompose upon heating into 2 molecules of potassium chloride and 3 molecules of oxygen, the latter escaping as a gas ( ↑ ). A picture of this would be



Hereafter, all chemical changes will be expressed by means of such balanced equations. The majority of these changes have been classified into four categories, which are illustrated in sections 23–26.

**23. Combination.—When two substances unite to form a third substance, the chemical reaction is called combination:**

$$A + B \rightarrow C.$$

DEMONSTRATION 4. COMBINATION: MAGNESIUM AND OXYGEN

Materials: Magnesium ribbon, forceps, burner.

The magnesium ribbon burns, uniting with oxygen in the air to form magnesium oxide, a white powder. A blinding white light and intense heat are given off. This reaction occurs in some photoflash bulbs and tracer bullets.

At the outset it is important to learn that chemical combination takes place between definite weights of substances to form a definite weight of the product. By burning a known weight of magnesium in a crucible and then weighing the oxide formed, chemists have found that 1 part by weight of magnesium combines with 0.66 part of oxygen to form 1.66 parts of the oxide. Let us examine this ratio 1 : 0.66 : 1.66 a little further. From our study of formulas we should have predicted that the compound MgO would be formed from the elements magnesium and oxygen. Their atomic weights, as will be seen from the table on the back cover of this text, are Mg = 24.32, O = 16, whence MgO = 24.32 + 16 = 40.32. The ratio of these weights is the same as the ratio given above, namely

$24.32 \div 24.32 = 1$; $16 \div 24.32 = 0.66$; and $40.32 \div 24.32 = 1.66$. In other words, we could have predicted the combining weights of these elements from a knowledge of their valences and atomic weights. Expressed in equation form this becomes

$$\begin{array}{ccccc} \text{magnesium} & + & \text{oxygen} & \rightarrow & \text{magnesium oxide;} \\ 2Mg & + & O_2 & \rightarrow & 2MgO; \\ 2(24.32) & + & 2(16) & \rightarrow & 2(24.32 + 16) \end{array}$$

which is the same ratio as

$$1 \quad + \quad 0.66 \quad \rightarrow \quad 1.66.$$

**Another Illustration of Combination: Iron and Sulfur.** The following experiment illustrates this further.

### DEMONSTRATION 5. COMBINATION: IRON AND SULFUR

Materials: Seven test-tubes, iron filings, flowers of sulfur, dilute hydrochloric acid, carbon disulfide (rhombic sulfur as an exhibit), magnet, mortar and pestle, filter paper, magnifying glass, funnel, burner, evaporating dish in hood.

Iron filings and sulfur have very different properties. Iron is magnetic and reacts with dilute hydrochloric acid, forming hydrogen (a colorless gas) and ferrous chloride. Sulfur is not magnetic and is insoluble in dilute hydrochloric acid, but readily soluble in liquid carbon disulfide, in which iron is insoluble. Sulfur also has a definite crystalline form.

When iron filings and sulfur are thoroughly ground together in a mortar, a greenish-black powder is obtained, which differs in appearance from either of the components. When the powder is tested, however, the iron and the sulfur are found to be present as such. Thus, the iron in the mixture is attracted by a magnet, and reacts with hydrochloric acid, leaving sulfur (yellow). When a portion of the powder is shaken in a test-tube with carbon disulfide and the contents of the tube poured into a folded filter paper, iron is left on the filter. By allowing the liquid to evaporate at room temperature in a dish [hood], sulfur is obtained, showing that we are dealing with a mixture.

If another portion of the original mixture is heated in a test-tube until the mass glows, a deep-seated change will take place. When the test-tube is allowed to cool and the material in it examined, it is found to be black, porous, non-magnetic, and insoluble in carbon disulfide. Close examination with a lens or a microscope does not reveal the presence of either iron or sulfur. When a portion of the solid is treated with dilute hydrochloric acid, hydrogen sulfide, a gas possessing a disagreeable odor, is evolved. The product formed is known as ferrous sulfide:

$$\begin{array}{l}
\text{iron} + \text{sulfur} \rightarrow \text{ferrous sulfide} \\
\text{Fe} + \text{S} \rightarrow \text{FeS} \\
55.85\text{ g.} + 32.06\text{ g.} \rightarrow 87.91\text{ g.} \quad \text{(weights).}
\end{array}$$

*Problem:* How many grams of iron would be required to unite with 64.12 grams of sulfur, and what weight of ferrous sulfide would be obtained? *Ans.* 111.70 g.; 175.82 g.

**24. Decomposition.—When a compound breaks down into two or more substances, the chemical reaction is called decomposition.** It is the reverse of combination:

$$C \rightarrow A + B.$$

DEMONSTRATION 6. DECOMPOSITION OF MERCURIC OXIDE

Materials: Hard glass test-tube, splinter, mercuric oxide, burner.

When red oxide of mercury (mercuric oxide) is heated in a test-tube, a gas is liberated which causes a glowing splinter to burst into flame. The colorless gas formed is a good supporter of combustion; it is oxygen. During the heating a shining mirror forms on the sides of the tube, and in the course of a few minutes the bright substance appears as globules. It is readily recognized as the metal mercury, or quicksilver. The equation for the reaction, and the weights of substances involved, are:

$$\begin{array}{ccccc}
\text{mercuric oxide} & \rightarrow & \text{mercury} & + & \text{oxygen} \\
2HgO & \rightarrow & 2Hg & + & O_2 \uparrow \\
2(216.61)\text{g.} & \rightarrow & 2(200.61)\text{g.} & + & 2(16)\text{g.}
\end{array}$$

*Problem:* How many grams of oxygen may be prepared by heating 100 grams of mercuric oxide. *Ans.* 7.39 grams.

**25. Displacement.—When an element reacts with a compound to form another element and another compound, the chemical reaction is called displacement:**

$$A + BC \rightarrow B + AC.$$

DEMONSTRATION 7. DISPLACEMENT OF COPPER BY IRON

Materials: Beaker-full of copper sulfate solution, iron knife or spatula.

When iron is dipped into copper sulfate, some of the iron goes into solution to displace the copper, and the spatula soon becomes coated with the red metal copper.

iron + copper sulfate → copper + iron sulfate.

$$\underset{}{Fe} + CuSO_4 \rightarrow \underset{\text{precipitates}}{Cu\downarrow} + \underset{\text{in solution}}{FeSO_4}$$

Notice that the metal, iron, displaces the metal, copper. The reader has already been cautioned against expecting the formation of a compound such as FeCu.

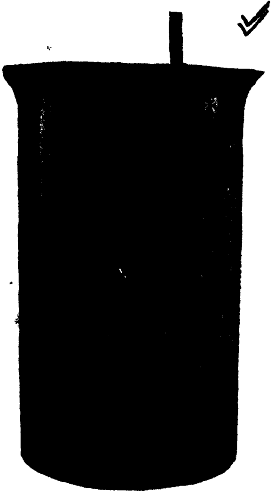


Fig. 6. A silver tree. A porous bag containing mercury is suspended in a water solution of a silver salt. Mercury *displaces* silver.

### ✓ DEMONSTRATION 8. DISPLACEMENT OF SILVER BY MERCURY, AND OF LEAD BY ZINC

Materials: Mercury in a cloth bag suspended in a beaker-full of silver nitrate solution. Zinc rod suspended in lead acetate solution.

In a few hours, interesting lead and silver trees will be seen in the two beakers (Fig. 6). The following **displacement** reactions will have occurred:

mercury + silver nitrate
→ silver + mercury nitrate;
zinc + lead acetate
→ lead + zinc acetate.

**26. Double Decomposition.—When two compounds react to form two other compounds, the chemical reaction is called double decomposition, or metathesis:**

$$AB + CD \rightarrow AD + CB.$$

### DEMONSTRATION 9. DOUBLE DECOMPOSITION

Materials: Test glass, filter paper, funnel, filter stand, stirring rod, evaporating dish on tripod over burner, water solutions of silver nitrate and sodium chloride.

When the two solutions are mixed, curdy white silver chloride separates out (precipitates, since silver chloride is insoluble in water):

silver nitrate + sodium chloride → silver chloride + sodium nitrate.

$$AgNO_3 + NaCl \rightarrow \underset{\text{precipitates}}{AgCl\downarrow} + \underset{\text{in solution}}{NaNO_3}$$

The silver chloride may be caught on the filter paper in the funnel; the filtrate which runs through the paper contains the sodium nitrate in solution. The sodium nitrate, too, may be recovered by evaporating the filtrate to dryness. Sodium nitrate is Chile saltpeter, natural source of explosives and fertilizers. Silver chloride is used on photographic film and paper since it decomposes and turns dark upon exposure to light. In fact an examination of the precipitate on the filter paper will show that the surface has already darkened in the sunlight.

Notice that in double decomposition the metal links with a non-metal. Again the reader is cautioned that a compound such as AgNa never forms in reactions such as these.

**Reading References:** Articles number 59, 210, 227, 423 in the Appendix.

## QUESTION REVIEW

I. Physical changes (21).

1. State which of the following changes are physical: rusting of iron, melting of snow, liquefaction of air, decay of vegetable matter, digestion of food, explosion of dynamite, crushing of rock, formation of dew, souring of milk, and the magnetization of iron.
2. Do physical changes always accompany chemical changes?

II. Chemical changes.

**a. Writing of equations (22).**

3. Is the transformation of ice into liquid water physical or chemical?
4. Name 5 physical and 5 chemical changes.
5. In terms of the atomic theory, distinguish between a physical and a chemical change.
6. After two or more substances are brought into contact how would you know whether they interacted chemically or simply remained mechanically mixed?
7. Write balanced equations illustrating the combination of each of the following elements with oxygen: Na, Mg, K, Al, Cu to form cupric oxide, Hg to form mercuric oxide, Zn, P to form the pentoxide, C to form the dioxide.
8. Express in words the changes shown in the following equations.

*a.* $2Na + Cl_2 \rightarrow 2NaCl$
*b.* $4P + 3O_2 \rightarrow 2P_2O_3$
*c.* $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu \downarrow$

**b. Varieties of chemical change. Combination (23). Decomposition (24). Displacement (25). Double decomposition (26).**

9. Define and illustrate with equations the four varieties of chemical change.
10. How many grams of iron would be required to unite with 64.12 grams of sulfur? What weight of ferrous sulfide would be obtained (atomic weights Fe 55.85; S 32.06)?
11. How many grams of oxygen may be prepared by heating 100 grams of mercuric oxide (atomic weights Hg 200.61, O 16)?

## CHAPTER IV

## OXYGEN

**27. Abundance and Importance of Oxygen.**—Owing to the great abundance, wide occurrence, and chemical activity of oxygen, it is a suitable element with which to commence the systematic study of the elements and their more important compounds.

Oxygen constitutes about one-fifth of the air by volume, of which it is the active component. We are dependent upon oxygen for heat and light and even life itself. We could not build a fire without it, and the gas is consumed in every breath we take. We therefore see that oxygen is of the highest importance.

**28. General Plan of Study.**—In study, it is always well to have a systematic plan. In our study of the chemical elements the following plan will, in general, be followed:

(*a*) History.
(*b*) Occurrence and Sources.
(*c*) Preparation.
(*d*) Physical Properties.
(*e*) Chemical Properties.
(*f*) Uses.

The most important compounds containing the particular element will also receive consideration.

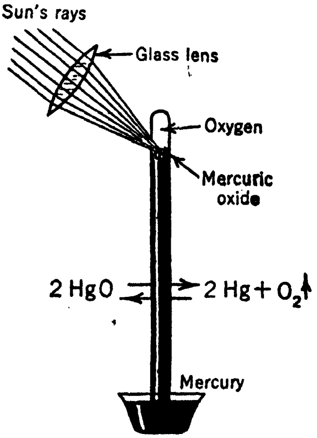


FIG. 7. Priestley's method for preparing oxygen.

**29. History of Oxygen.**—Joseph Priestley, an English chemist and clergyman, is usually regarded as the discoverer of oxygen. He prepared it, August 1, 1774, by heating mercuric oxide ("red precipitate") confined over mercury in an elongated glass vessel, the heat being obtained by the concentration of the sun's rays by means of a lens (Fig. 7). (Demonstration 6, section 24.)

The reaction was

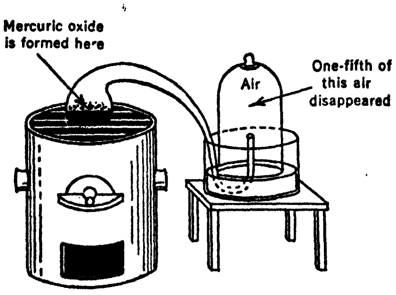
$$2HgO \rightarrow 2Hg + O_2.$$

red oxide → mercury + oxygen

Priestley observed that a lighted candle burned more brightly in the new gas (oxygen) than in air. Even previous to this K. W.

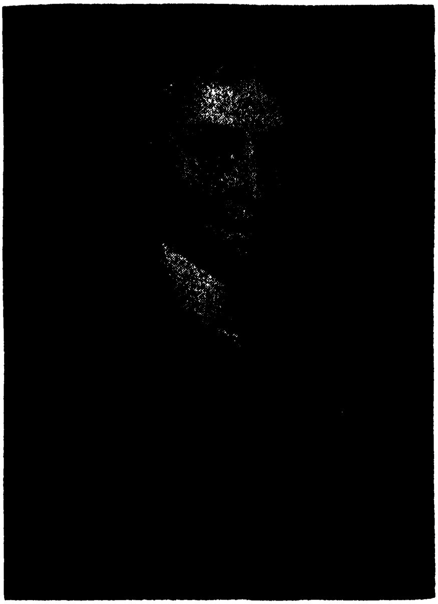
Scheele, an impoverished Swedish apothecary, had prepared oxygen (1771–1772); but since he did not publish the results of his researches until 1777 he is not given priority credit. Scheele heated various substances, such as barium oxide and saltpeter; and his research with black manganese dioxide was a brilliant piece of work. During this investigation he discovered chlorine, oxygen, manganese, and barium dioxide. Despite his limited facilities for experimenting, Scheele was one of the greatest chemists of all time.

Antoine Laurent Lavoisier, renowned French chemist, took up the study of the properties of oxygen, and in 1777 carried out his classical experiment to show the relation of the gas to air. By means of a charcoal fire he heated mercury confined in a retort, the neck of which passed up through a vessel containing mercury into a bell-jar with air in it (Fig. 8). The mercury and air were heated for 12 days, at the end of which time Lavoisier observed that a red powder was formed on the surface of the mercury, and the air had lost about one-fifth of its volume. (50 cubic inches of air was reduced to about 42 cubic inches, approximately 8 cubic inches (50–42) having combined with the mercury.) He then removed the red powder from the retort and heated it in another vessel; it yielded a volume of an active gas equal to the decrease in the volume (about 8 cubic inches) of the original air. This gas, Lavoisier found, behaved exactly like Priestley's oxygen. On the other hand, the gas left in the retort would not combine with mercury; it extinguished a burning candle, and a mouse was quickly suffocated in it. Lavoisier named this second gas *azote* (**nitrogen**). The proof was now complete that oxygen and nitrogen were components of the air. Subsequently Lavoisier named the active component **oxygen** (Greek, *acid-producer*), for he thought it was an essential constituent of all acids. This word is a misnomer, however, for there are acids, *e.g.*, hydrochloric acid (HCl), that contain no oxygen.



$$2Hg + O_2 \longrightarrow 2HgO$$

FIG. 8. Lavoisier's experiment which proved that air was one-fifth oxygen.

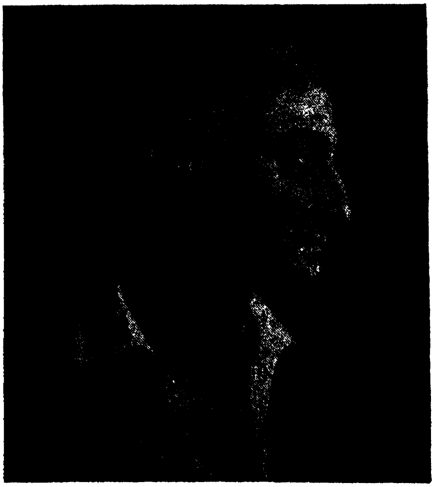


**Joseph Priestley**
(1733–1804)

Priestley was a clergyman, teacher, writer, and chemist. He was endowed with an unusual gift for experimenting and observing, and *he prepared and investigated many gases*, such as oxygen, hydrogen chloride, ammonia, and sulfur dioxide. The *discovery of oxygen* was his most important contribution to science. Emigrated to America in 1794, and lived at Northumberland, Pennsylvania. He was a staunch supporter of the *phlogiston theory*.

**Antoine Laurent Lavoisier** (1743–1794)

A great investigator and prolific writer, he proved that combustion, calcination and respiration are dependent upon oxygen; also that oxygen is a component of the air. By his experiments he proved that matter is indestructible (1774). He became associated with the Farmers General, and was very unjustly beheaded in 1794. He bitterly assailed the *phlogiston theory*.



**30. Collapse of the Theory of Phlogiston.**—The discovery of oxygen overthrew an erroneous theory of combustion which had ruled chemical thought for nearly a hundred years. This theory, the theory of phlogiston (see section 8), postulated the existence of a fire-stuff, **phlogiston,** which escaped with a whirling motion from burning bodies. J. J. Becher (1635–1682) and George Ernst Stahl (1660–1734), chief proponents of the theory, explained the combustion of a metal in the following way:

$$\text{metal} \rightarrow \underset{\substack{\textit{which is}\\ \textit{a white ash}}}{\text{calx}} + \underset{\substack{\textit{which}\\ \textit{escapes}}}{\text{phlogiston}} \uparrow. \tag{1}$$

The modern explanation is:

$$\text{metal} + \text{oxygen} \rightarrow \underset{\textit{a white ash}}{\text{metal oxide}}. \tag{2}$$

To the phlogistians a combustible substance such as coal, which left relatively little ash, was supposed to be so rich in phlogiston that practically all of it escaped during burning. For many decades this concept of phlogiston pervaded all chemical thought. It met many difficulties. No one had ever seen phlogiston. No one knew exactly what phlogiston was. Moreover it was known that the product formed from burning a metal weighed *more* than the original metal. Today this result seems inevitable since according to equation (2) above, the metal has added oxygen from the air. But to explain it in terms of the phlogiston theory (equation 1) it was necessary to argue that phlogiston had *negative weight*; consequently a metal gained in weight when it lost phlogiston!

With the discovery of oxygen the real explanation of combustion became obvious, and Lavoisier proposed the mechanism depicted in equation (2) above.

Despite the convincing simplicity of this modern concept it was opposed by many important contemporaries of Lavoisier. Even Priestley, discoverer of oxygen, continued to write bitterly in defense of the theory of phlogiston from his home in the New World at Northumberland, Pennsylvania, whither he had fled from England for political reasons during the French Revolution.

**31. Occurrence of Oxygen.**—In the free state, oxygen, as $O_2$, makes up about one-fifth of the air by volume and nearly one-fourth by weight. Present in water, as $H_2O$, it constitutes 85.79 per cent by weight of the oceans which cover the earth.

Because of the presence of oxygen gas everywhere, many **metallic oxide** ores, including the oxides of iron, copper, tin, aluminum, manganese and zinc, have been formed on the surface of the earth. It may be of some interest to describe oxides of iron in more detail. Most important and abundant of our iron ores is *ferric oxide*, or *hematite* (Greek, *blood-like*), red oxide of iron. Enormous quantities of this mineral are found in the Lake Superior region, where it is mined in large open quarries, since it lies near the surface. It is this same hematite that confers a red color upon certain soils and rocks: for example, the Grand Canyon in Arizona and Red Rock Canyon in California. Finely divided hematite is used very extensively as a pigment.

Several **oxides of non-metals**, too, occur in Nature in abundance. The sands of the sea are *silicon dioxide.* This same compound, $SiO_2$, occurs as quartz in many forms. Rock crystal is a clear colorless form of it. Amethyst is a quartz tinted violet by traces of impurities, and is used for making ornamental objects. *Carbon dioxide,* another non-metallic oxide, is always present in specimens of natural air; it also occurs in natural waters, the soil, and escapes through vents and fissures of the earth's crust in certain localities.

In addition to these oxides of metals and non-metals, oxygen is widely distributed throughout Nature in various other **compounds.** These include *carbonates* (*e.g.*, pearls, limestone and chalk are calcium carbonate, $CaCO_3$), *nitrates* (*e.g.*, Chile saltpeter is sodium nitrate, $NaNO_3$), *sulfates* (*e.g.*, gypsum is calcium sulfate, $CaSO_4$), and *silicates* (*e.g.*, feldspars are complex silicates such as $KAlSi_3O_8$).

Indeed, oxygen is our most abundant element, comprising 50 per cent by weight of the earth's shell and atmosphere.

**32. Preparation of Oxygen.**—Oxygen is prepared by a number of industrial processes. Each manufacturer must decide which method is most suited to his own needs from considerations of simplicity of operation, utilization of by-products, purity, availability of raw materials, proprietary patent rights, and other factors which affect operating costs. In the laboratory, on the other hand, the quantities of gas required are usually so small that cost is of secondary importance. While the methods outlined below include several of historical or academic interest, the chief preparation methods today are

**Industrial: (a) from liquid air, (b) by the electrolysis of water;**

**Laboratory: (a) purification of industrial, tank oxygen, (b) laboratory electrolysis of water, (c) heating potassium chlorate or potassium permanganate.**

### DEMONSTRATION 10. LABORATORY PREPARATIONS OF OXYGEN

Materials: hard glass test-tubes, burner, test-tube holder, splinters, mercuric oxide, barium peroxide, hydrogen peroxide, manganese dioxide, sodium peroxide.

Oxygen may be prepared by the following methods.

## a. Preparation of Oxygen by Heating Oxides and Compounds Rich in Oxygen

(1) **By heating the oxides of the more inactive metals,** such as those of mercury, silver, gold, and those of the platinum metals. Priestley obtained it by heating mercuric oxide:

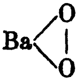
$$\underset{\text{Mercuric oxide}}{2HgO} \underset{\text{warm}}{\overset{\text{hot}}{\rightleftarrows}} \underset{\text{Mercury}}{2Hg} + \underset{\text{Oxygen}}{O_2\uparrow}.$$

This method is of historical interest, but is too expensive. The action is **reversible,** for HgO can be formed by heating mercury in air.

(2) **By heating higher oxides.**

Note: *higher oxides* has the following meaning. For metals with variable valence such as Mn which forms MnO and $MnO_2$, the latter would be the higher oxide. For metals with constant valence, such as Na, Ba, H, a higher oxide, called a **peroxide**, forms. Thus in addition to the normal oxides $Na_2O$, sodium oxide, BaO, barium oxide, and $H_2O$, water, these elements form the peroxides $Na_2O_2$, sodium peroxide, $BaO_2$, barium peroxide, and $H_2O_2$, hydrogen peroxide. Valences apparently do not balance in these compounds; actually, however, the atoms are held together by the same number of bonds as the number of valences the atom normally possesses. Thus we may picture the compounds

Na—O—O—Na H—O—O—H



in which sodium and hydrogen have their normal valence of 1 and barium and oxygen their usual valence of 2. The structure —O—O— is called the peroxide structure.

Oxygen cannot be prepared by heating the lower oxides of metals other than those mentioned above, but it may be obtained by heating certain higher oxides.

$$\begin{array}{cccc} 2BaO_2 & \underset{500^\circ}{\overset{1000^\circ}{\rightleftarrows}} & 2BaO & + O_2. \\ \text{Barium peroxide} & & \text{Barium monoxide} & \end{array}$$

**Brin's process**, based upon this reaction, was once an important industrial source of oxygen. However, pressure instead of temperature was used in driving the reaction in one direction or the other. Operating constantly at 700° C., Brin formed $BaO_2$ from BaO and air at 3 atmospheres pressure; and then eventually removed one atom of oxygen from the $BaO_2$ by reducing the pressure.

Hydrogen peroxide ($H_2O_2$) readily loses oxygen to form water. In fact, were it not that the drug-store variety of hydrogen peroxide contains a preservative, it would decompose into water in a few hours:

$$2H_2O_2 \rightarrow 2H_2O + O_2.$$

(3) **By heating certain compounds rich in oxygen**, such as chlorates, certain nitrates, or potassium permanganate. The gas can be liberated by heating a small quantity of potassium chlorate in a hard glass test-tube. The white crystals melt at 357°, and at 380° bubbles of oxygen are evolved. A glowing splinter thrust into the tube burns brilliantly. The chemical change is:

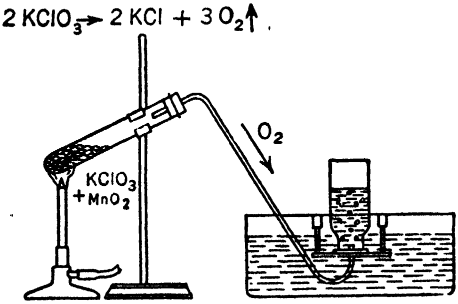


FIG. 9. Preparation of oxygen.

$$\begin{array}{ccccc} 2KClO_3 & \rightarrow & 2KCl & + & 3O_2. \\ 2 \times 122.6\text{ g.} & & 2 \times 74.6\text{ g.} & & 3 \times 32\text{ g.} \\ \text{Potassium chlorate} & & \text{Potassium chloride} & & \end{array}$$

This equation shows that 96 g. of oxygen may be obtained by heating 245.2 g. (2 gram-molecular weights) of potassium chlorate.

The production of oxygen is greatly accelerated by mixing the potassium chlorate with manganese dioxide ($MnO_2$). The manganese dioxide undergoes no permanent change, and it may be recovered at the end of the action by dissolving the potassium chloride in water. The mere presence, then, of manganese dioxide increases the speed of the reaction, and the generation of oxygen is accomplished at a much lower temperature—below 200°.

### DEMONSTRATION 11. PREPARATION OF OXYGEN FROM POTASSIUM CHLORATE

Materials: 10 g. of potassium chlorate in hard glass test-tube over burner, delivery tube and trough to collect oxygen (Fig. 9), 10 g. $KClO_3$ plus 2 g. $MnO_2$. **Warning.**—Manganese dioxide is sometimes adulterated with organic matter, which may cause a violent explosion when heated with potassium chlorate! It may be tested before using by heating half a gram of it mixed with an equal weight of the chlorate.

It should be clearly understood that there are numerous oxides and other oxygen compounds which do not yield oxygen when heated, *e.g.*, calcium oxide ($CaO$), silicon dioxide ($SiO_2$), and calcium carbonate ($CaCO_3$).

### b. Preparation by the Interaction of Sodium Peroxide and Water

Oxygen may be prepared in the laboratory by dripping water from a dropping funnel upon sodium peroxide (*oxone*):

$$\underset{\text{Sodium peroxide}}{2Na_2O_2} + 2H_2O \rightarrow \underset{\text{Sodium hydroxide}}{4NaOH} + O_2.$$

### c. Commercial Preparation from Liquid Air

Most commercial oxygen, approximately two billion cubic feet a year, is prepared by the fractional distillation of air. Air is compressed to about 200 atmospheres pressure and then allowed to expand. This cools the air. The cycle is repeated thrice, by which time liquid air is formed. If this liquid is allowed to evaporate, nitrogen which is more volatile (B.P. −195.8° C.) escapes first, leaving oxygen (B.P. −183.0° C.) behind. The oxygen (95–99 per cent pure) is compressed into strong steel cylinders at about 120 atmospheres of pressure.

DEMONSTRATION 12. EVAPORATION OF LIQUID AIR

Materials: Tall cylinder nearly full of water, splinter, burner, 20 cc. liquid air.

When liquid air is poured on water the nitrogen-oxygen mixture floats. Nitrogen boils away first leaving chiefly oxygen, which may be tested with a glowing splint. When liquid oxygen alone remains it sinks, since its density is greater than that of water. This experiment demonstrates the separating of air into nitrogen and oxygen (Fig. 10).

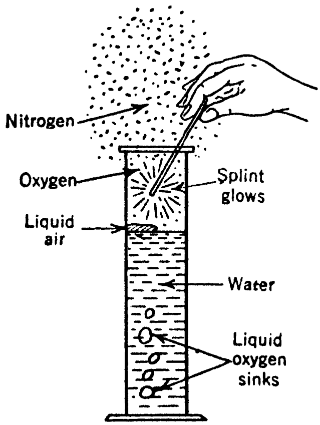
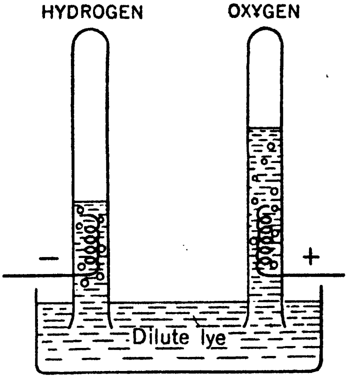


FIG. 10. Evaporation of liquid air separates nitrogen from oxygen. (Demonstration 12.)



$$2\,H_2O \longrightarrow 2\,H_2\uparrow + O_2\uparrow$$

FIG. 11. Electrolysis of water.

## d. Preparation by Electrolysis of Water

DEMONSTRATION 13. ELECTROLYSIS OF WATER

Materials: Two test-tubes, 30-cm. crystallizing dish, 10-volt D.C. current with copper wire electrodes, dilute sulfuric acid, dilute sodium hydroxide, splinters.

Water may be separated into its constituent elements, hydrogen and oxygen, by passing an electric current through it (Fig. 11). This process of decomposition by the use of the electric current is called **electrolysis** (Greek, meaning *decomposition by electricity*). It is a source of very pure hydrogen which is given off at the negative pole (the **cathode**), and pure oxygen which is given off at the positive pole (the **anode**).

In actual practice pure water is too poor a conductor of electricity, so that acid or an hydroxide is added in small amounts. In industry the electrolysis is carried out with a solution of lye (sodium hydroxide, NaOH) in iron tanks; and in the research laboratory a convenient apparatus consists of two concentric tubes containing two electrodes of coiled nickel or iron wire in sodium hydroxide. Industrially the process is feasible only when the manufacturer has a need for very pure hydrogen and oxygen; for it is twice as expensive as the preparation by the liquefaction of air.

**33. Catalysis.**—The presence of small quantities of certain substances alters the rate of many chemical reactions. Thus the presence of oxides of manganese, iron and copper accelerate the decomposition of potassium chlorate; finely divided manganese dioxide will cause the rapid evolution of oxygen from hydrogen peroxide; and ozone is changed into oxygen when brought in contact with platinum black. In none of these cases is the metallic oxide or the metal permanently changed. Nor do they start the chemical reaction; they merely increase the rate or speed of change. For substances such as these Berzelius proposed the name **catalysts**; and for their action, **catalysis** (Greek, meaning *breaking down,* or *decomposition*). Both positive and negative catalysts are known, although in the latter case the term **inhibitor** is applied for it has been found that many of the so-called "negative catalysts" are changed into other substances during the reaction. Inhibitors keep our catsup from souring, our butter from turning rancid, our automobile tires from cracking, our gasoline from knocking, and our hydrogen peroxide from decomposing into water and oxygen.

Enzymes and hormones are *biological catalysts.* One enzyme splits starch, another splits proteins, and still another splits fats. Hormones control our sex, our growth, our metabolism.

Industrial catalysis has made possible our civilization of today. High octane gasoline, sulfuric acid, synthetic ammonia, hydrogenated oils, alcohols, sugar from wood, and fats from coal are a few products which owe their existence to the action of catalysts.

### DEMONSTRATION 14. CATALYSIS

**Materials:** Manganese dioxide, test-tube, splinter, hydrogen peroxide.

Manganese dioxide added to 10 cc. of hydrogen peroxide catalyzes its decomposition into water and oxygen. Evolution of the latter can be demonstrated with the glowing splint.

**34. Atomic and Physical Properties of Oxygen.**—The scheme presented in table 8 will be adopted throughout this text. The meaning of each property will be apparent from the description of oxygen following the table. The significance of atomic weight (at. wt.), atomic number (at. no.), electronic arrangement, isotopes and diameter of ions will be explained later in the text and are included here only for subsequent reference.

TABLE 8. ATOMIC AND PHYSICAL PROPERTIES OF OXYGEN

| | | | |
|---|---|---|---|
| at. wt. | 16.0000 | $d_{O_2\ gas}$ | 0.00142900 |
| at. no. | 8 | $d_{Oxygen\ liq.}$ | 1.13 |
| electronic arrangement | $1s^2 2s^2 2p^6$ | B.P. | −183.0° C. |
| isotopes | 16, traces of 17, 18 | M.P. | −218.7° C. |
| diameter $O^{=}$ in crystals | 1.40 A° | C.T. | −118° C. |
| | | C.P. | 50 atmos. |
| | | Solubility per 100 cc. water at | |
| | | 0° C. | 4.89 cc. |
| | | 20° C. | 3.10 cc. |

Oxygen at room temperature is a colorless, odorless, tasteless gas. The weight of one cubic centimeter of the gas at 0° and 1 atmosphere pressure is 0.00142900 gram, called its density (*d*). Liquid oxygen has a pale blue color, is strongly magnetic, and is heavier than water (density 1.13; $dH_2O_{liq.} = 1.0$). The melting point (M.P.) and boiling point (B.P.) are given for a pressure of 1 atmosphere. At −118° C. oxygen will liquify at a pressure of 50 atmospheres; it will not liquefy above this temperature no matter how much pressure is applied. These critical conditions are called the critical temperature (C.T.) and critical pressure (C.P.). Dewar froze oxygen to a pale-blue solid by cooling liquid oxygen with liquid hydrogen. The solubility of oxygen in sea-water is about 78 per cent of that in pure water; fish are dependent upon this dissolved oxygen.

**35. Chemical Properties of Oxygen.**—In the study of the chemical properties of a substance, we shall consider its ability to interact with other substances, the conditions under which the chemical actions occur, the speed of the actions, the properties and composition of the products formed, and the energy changes accompanying the chemical changes.

Oxygen is a very active element, particularly at high temperatures, for it enters into vigorous combination with many different substances. It has chemical properties similar to those of the air, but it is much more active, being a powerful supporter of combustion.

### DEMONSTRATION 15. OXYGEN REACTIONS

Materials: Six bottles of oxygen, 4 deflagrating spoons, burner, blue litmus paper, red litmus paper, tongs, flowers of sulfur, charcoal, white phosphorus, magnesium ribbon, sodium, 6″ length of iron picture wire with tip wrapped with cotton cord and dipped into moistened flowers of sulfur, mortar filled with soapy water, tank hydrogen and oxygen with rubber tubes.

Show the combination of oxygen with the following elements.

### a. Oxygen and the Non-Metals

Oxygen enters into direct combination with all the non-metals, excepting the halogens and the inactive gases of the atmosphere.

(1) When burning sulfur contained in a deflagrating spoon is thrust into oxygen, it burns more vigorously, forming sulfur dioxide, a colorless gas with a sharp odor:

$$S + O_2 \rightarrow SO_2.$$

Sulfur dioxide dissolves freely in water, forming sulfurous acid:

$$H_2O + SO_2 \rightleftarrows \underset{\text{Sulfurous acid}}{H_2SO_3}.$$

The solution has a sour taste and turns blue litmus red, which is a characteristic of a class of compounds called **acids.**

**Fundamental fact: Oxides of certain non-metallic elements interact with water to form acids, which turn blue litmus red.**

(2) When finely divided charcoal (carbon) is heated in an iron pan and poured into a jar of oxygen (*Care!*), it burns brilliantly, forming carbon dioxide:

$$C + O_2 \rightarrow CO_2.$$

Carbon dioxide, like sulfur dioxide, dissolves in water, forming a weak, unstable acid:

$$H_2O + CO_2 \rightleftarrows \underset{\text{Carbonic acid}}{H_2CO_3}.$$

(3) When a very small piece of white phosphorus is heated carefully in a deflagrating spoon and then plunged into a jar of

oxygen, it burns with the production of intense heat and light, forming phosphorus pentoxide ($P_2O_5$):

$$4P + 5O_2 \rightarrow 2P_2O_5.$$

Phosphorus pentoxide forms a white smoke, which gradually dissolves in water, finally forming phosphoric acid ($H_3PO_4$).

**Warning.**—*Great care must be exercised in handling white phosphorus!*

### b. Oxygen and the Metals

All familiar metals, excepting silver, gold, and the platinum metals, when heated, unite with oxygen.

The alkali and the alkaline earth metals are the most active of the metals, and they unite readily with oxygen, forming metallic oxides. When a magnesium ribbon is heated in the flame of a burner, and then thrust into a vessel containing oxygen, it burns with dazzling brilliancy, forming magnesium oxide, or magnesia, MgO:

$$2Mg + O_2 \rightarrow 2MgO.$$

Magnesium oxide is a white powder and is sparingly soluble in water. When thoroughly treated with water, it forms a very dilute solution of magnesium hydroxide:

$$MgO + H_2O \rightleftarrows Mg(OH)_2.$$

Metallic hydroxides have a soapy taste and the general characteristic of turning red litmus blue. Acids and hydroxides are very different in their chemical conduct.

**Fundamental fact: Oxides of the more active metals interact with water, forming metallic hydroxides.**

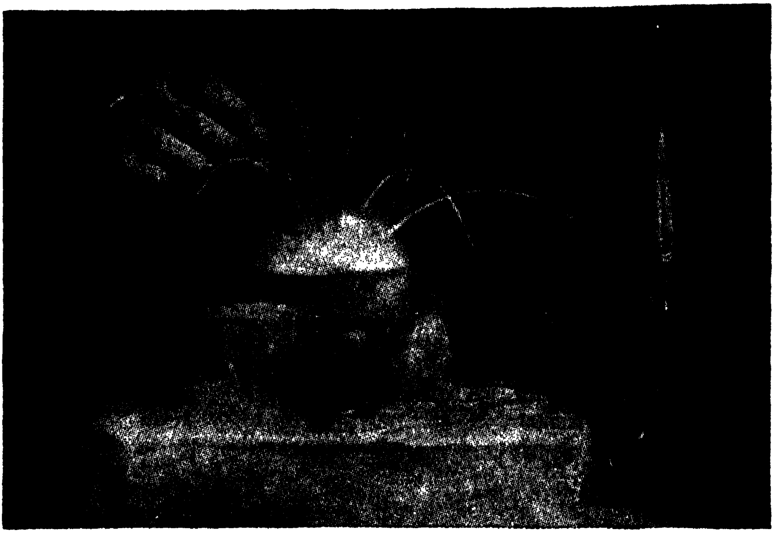
Some other very important metallic hydroxides follow.

| *Oxide of Metal* | *Water* | *Metallic hydroxide* |
|---|---|---|
| $Na_2O$ | $+ H_2O \rightarrow 2NaOH$, | Sodium hydroxide |
| $K_2O$ | $+ H_2O \rightarrow 2KOH$, | Potassium hydroxide |
| CaO (lime) | $+ H_2O \rightleftarrows Ca(OH)_2$, | Calcium hydroxide |

Iron will burn in an atmosphere of oxygen. This may be shown by coating the end of a bundle of fine iron wire with sulfur, igniting the latter, and then thrusting the bundle into a jar of oxygen (Fig. 12). The metal burns with brilliancy, forming *magnetic oxide of iron:*

$$3Fe + 2O_2 \rightarrow Fe_3O_4.$$

The oxides of iron are FeO, ferrous oxide; $Fe_2O_3$, ferric oxide; and $Fe_3O_4$, magnetic oxide of iron. In this latter compound both valences of iron occur, *i.e.*, $\overset{+2}{Fe}(\overset{+3}{Fe}O_2)_2$ so that this might be called ferrous ferrite. This magnetic oxide of iron is identical with hammer scale; it is a black, brittle substance and entirely different from *iron rust* (ferric oxide, $Fe_2O_3$). The oxides of iron are insoluble in water, as are most oxides of heavy metals. They do not therefore interact with water to form metallic hydroxides.



*From the Journal of Chemical Education, Courtesy Professor Cady.*

FIG. 12. Iron watch spring burning in liquid oxygen.

### c. Oxygen and Hydrogen

If these two gases are bubbled simultaneously through soapy water and a flame applied to the bubbles (*Care!*) a thunderous explosion occurs and water is formed:

$$2H_2 + O_2 \rightarrow 2H_2O.$$

Water will not affect litmus for it is neither just an acid nor just a hydroxide but, enigmatically enough, both, *viz.*, HOH. We say that it is *neutral.*

### SOME OXIDATIONS

**36. Some Oxidations.**—The combination of a substance with oxygen is called **oxidation.** That the term is a broad one will be seen from the numerous examples of oxidation which are described in the remainder of this chapter.

**37. Rusting of Metals.**

#### DEMONSTRATION 16. RUSTING

Materials: Steel wool or iron filings, test-tube, 400 cc. beaker half full of water.

The rusting of iron may be shown by sprinkling iron filings over the inside of a wet test-tube and then inverting it over water. In the course of a week about one-fifth of the gas confined in the tube disappears, and water rises to take its place. Not only does this experiment prove what rusting is, but it shows incidentally that about one-fifth of the air by volume is oxygen. Early chemists found considerable difficulty in explaining this phenomenon of rusting. It was known that the rusts (oxides) were heavier than the metals and it was supposed that something was taken from the air; but it was the Russian, Lomonossov, in 1756, who first proved experimentally that the extra substance did come from the air.

**38. Biological Oxidations.** The oxygen dissolved in water is very important in the disposal of sewage. The latter is mixed with large volumes of water, not simply to dilute the sewage but for the object of having it undergo oxidation by coming in contact with dissolved oxygen. Slow oxidation takes place in the bodies of animals. The oxygen of the inspired air combines with the **hemoglobin** in the red-blood corpuscles to form an unstable compound (*oxyhemoglobin*) which circulates throughout the body and oxidizes, to water and carbon dioxide, the hydrogen and carbon absorbed during digestion. During this oxidation process heat is given out, which is of the greatest importance in keeping the body warm; and whether the oxidation is slow or rapid, the same amount of heat is liberated in the two cases, provided that the same kinds and quantities of substances undergo oxidation.

Aviators flying at great heights need more oxygen than they can obtain from the air; therefore, they are supplied with cylinders of compressed oxygen and breathing helmets. This prevents their becoming "dopey." Self-contained oxygen breathing apparatus are employed in fighting mine fires and in rescuing miners trapped by fire or by poisonous gases (Fig. 13); and oxygen tents are used for pneumonia.

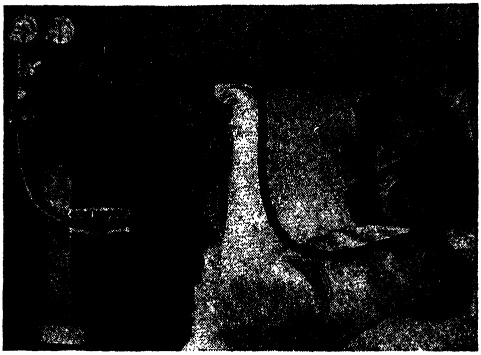


FIG. 13. Injector oxygen mask. Described in J. of Aviation Medicine, April, 1941. *Courtesy of Dr. Alvan L. Barach.*

**39. Combustion of Fuels.** Most fuels contain carbon and hydrogen, as the following general formulas will show: charcoal or coal, C; wood, $C_6H_{10}O_5$; alcohol, $C_2H_6O$; benzene, $C_6H_6$; gasoline, $C_8H_{18}$; kerosene, $C_{12}H_{26}$; Diesel fuel, $C_{15}H_{32}$; illuminating gas, $H_2$ and $CH_4$. Obviously when these burn in air the products are carbon dioxide and water.

DEMONSTRATION 17. PRODUCTS FROM THE COMBUSTION OF A CANDLE

Materials: Candle, large flat cork, 30-cm. crystallizing dish, cylinder, limewater.

That water and carbon dioxide are the products of a burning candle may easily be demonstrated by inverting a glass cylinder over a cork supporting a lighted candle. Moisture collects upon the glass. After the candle has gone out, the presence of carbon dioxide in the cylinder may be confirmed by adding a few cc. of limewater and shaking: carbon dioxide will form a milky white precipitate of calcium carbonate with limewater. If the experiment is repeated with the cork floating in a crystallizing dish containing water, the latter is sucked into the cylinder so that the cork rises as the oxygen is removed from the air and the carbon dioxide dissolves in the water (Fig. 14).

Heat is given off during combustion. We say that the reaction is **exothermic.** The quantity of heat given off is expressed in units called **calories,** in which one gram-calorie (abbreviation, cal.) is the amount of heat required to raise one gram of water one degree centigrade (from 15° C. to 16° C.). It is this same calorie which haunts the lives of the "somewhat stout," for when we say that a pound of butter furnishes approximately 4000 cals. and a pound of candy 1800 cals. we mean that that many units of heat energy are generated in the body by the oxidation of fats and sugars.

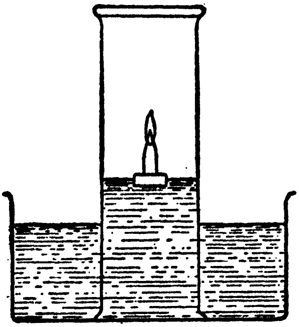


Fig. 14. Combustion of a candle in a closed container.

Engineers very commonly use the **British Thermal Unit** (B.T.U.). This is the amount of heat required to raise 1 pound of water 1° F., and equals 252 cals. The efficiency of your local city gas is judged by its B.T.U. rating.

Fig. 15. Oxy-acetylene welding of oil pipes.

By far the largest consumption of industrial oxygen is for cutting and welding metals by the oxyacetylene (3300° C.), oxyhydrogen (2800° C.), or oxyethylene blow-torch in construction work (Fig. 15). Here, advantage is taken of the large heats of combustion of these gases, *viz.*,

$$2H_2 + O_2 \rightarrow 2H_2O + 119{,}000 \text{ cals.}$$
$$2C_2H_2 + 5O_2 \rightarrow 2H_2O + 4CO_2 + 612{,}200 \text{ cals.}$$

This same heat of combustion is utilized in the blast furnace and steel converter for keeping the iron molten during the purifying process.

**40. Spontaneous Combustion.** Certain substances will catch fire in the air even at low temperatures. We say that their **kindling temperature** is low. Thus white phosphorus has a kindling temperature of 35° C., and zinc ethyl and the hydrides of silicon also catch fire spontaneously when exposed to air. Carbon disulfide has a kindling temperature of 150° C. whereas hydrogen ignites in air only above 550° C. However, the temperature at which ignition occurs depends upon pressure, fineness of material, catalytic agents, and other variables.

Why do coal, hay-stacks and greasy or oily rags sometimes ignite spontaneously? To answer this question it is necessary to realize two properties of these substances, namely that they (*a*) slowly unite with oxygen, giving off heat, and (*b*) are poor conductors of heat. Now a drop of oil exposed to the air will slowly oxidize and its heat of combustion is dissipated in the surrounding air. The same drop of oil confined within a rag, however, gives off the same quantity of heat; but since under these conditions the rag is a poor conductor of heat, the temperature of the material rises. And so combustion proceeds for months, until the kindling temperature is reached, when the oily rags, hay-stack, or coal bursts into flame. It is customary to sprinkle piles of coal with water containing an inhibitor, such as pyrogallol, to prevent this spontaneous combustion. An annual loss of $20,000,000 is suffered in the United States from spontaneous combustion.

**41. Dust Explosions. Rate of Oxidation.** An explosion is due to a very rapid chemical change resulting in a sudden large change in pressure. Some substances, like dynamite or T.N.T., vigorously decompose. Others, such as gas mixtures like gasoline and oxygen, ignite explosively. Lastly, finely divided organic matter such as charcoal, flour, starch, etc., suspended in the air can often explode if ignited by a flame or spark. This latter type of rapid combustion is known as a **dust explosion.**

### DEMONSTRATION 18. DUST EXPLOSION

Materials: 12-quart milk can fitted at the bottom with funnel and 4-foot rubber tube, candle suspended in can, lycopodium powder. See Fig. 16. Also, iron nail, tongs, burner, iron filings in salt shaker.

Place 10 cc. of lycopodium powder (spores of club-mosses) in the funnel and light the candle. Place the cover on the can and blow suddenly through the funnel. The powder scatters, followed by an explosion. Reaction has been so rapid because of the enormous surface, nearly an acre, of powder suddenly exposed to the air.

Some terrific explosions have occurred in flour mills, and so today the modern mills are equipped with elaborate installations to remove dust; and machinery likely to develop sparks of electricity by friction is grounded. In some dust explosions the speed of propagation of the flame has ranged from 2000 to 6000 feet per second, and pressures ranging from 270–400 pounds per square inch have been recorded (Fig. 17).

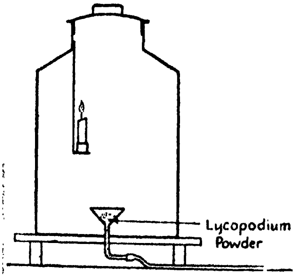


FIG. 16. Ready to demonstrate a dust explosion. (Demonstration 18.)

*Courtesy of Bureau of Agricultural Chemistry and Engineering, U. S. Department of Agriculture.*

FIG. 17. Fire following dust explosion in Chicago grain elevator. 9 lives lost, 30 people injured, property damage over $3,500,000, in this explosion.

Dust explosions are an interesting example of how the **speed of chemical reaction** may be increased by merely increasing the amount of surface exposed for reaction. In the same way, iron in the form of a bar rusts slowly when exposed to air, but burns rapidly and brilliantly when iron filings are sprinkled into the flame.

**42. Oxidizing Agents.**—We have already seen that some compounds part with oxygen rather readily, and are therefore used in the preparation of that gas. Moist sodium peroxide will set fire to paper; potassium nitrate is a component of ordinary gunpowder, so when a gun is fired the niter furnishes the oxygen which takes part in the combustion inside the gun; and it is known to all how readily hydrogen peroxide yields oxygen. The chemist can cause certain oxidations to take place by making use of these compounds which readily give up their oxygen. They are called **oxidizing agents.** A few important oxidizing agents follow.

| | |
|---|---|
| Hydrogen peroxide, | $H_2O_2$ |
| Potassium chlorate, | $KClO_3$ |
| Sodium peroxide, | $Na_2O_2$ |
| Potassium nitrate, | $KNO_3$ |
| Nitric acid, | $HNO_3$ |
| Potassium permanganate, | $KMnO_4$ |

**Reading References:** Articles number 4, 29, 32, 102, 119, 205, 309, 403, 408, 410, 423 in the Appendix.

## QUESTION REVIEW

**Abundance and importance of oxygen (27).**

**General plan of study (28).**

### I. HISTORY OF OXYGEN.

**a. General (29).**

1. Who discovered oxygen? Who first prepared it? Who demonstrated its importance in combustion?
2. Outline Lavoisier's proof of the composition of air.
3. Why is *oxygen* a misnomer?

**b. Collapse of the theory of phlogiston (30).**

4. Contrast the explanation of combustion given by the phlogistians with that proposed by Lavoisier.
5. What were some of the objections to phlogiston?

### II. OCCURRENCE OF OXYGEN (31).

6. Describe the oxides of iron (refer to the Index).
7. Describe 2 oxides of non-metals found in Nature.
8. Name 4 types of oxygen compounds other than oxides found in Nature.

### III. PREPARATION OF OXYGEN.

**a. Laboratory and industrial methods (32).**

9. Why may industrial methods for preparing oxygen be unsuitable for the laboratory, and vice versa?
10. List 2 most important industrial methods and 2 important laboratory methods for preparing oxygen.
11. Give one example each showing oxygen being prepared from (1) an oxide of an inactive metal, (2) a higher oxide, (3) other compounds containing oxygen.
12. Which of the following materials will yield oxygen upon heating: $HgO$, $CaO$, $SiO_2$, $MgO$, $MnO_2$, $H_2O$, $H_2O_2$, $CaCO_3$, $KClO_3$, $KNO_3$, $Ag_2O$, $BaO$, $BaO_2$?
13. Describe the commercial production of oxygen from liquid air. How is commercial oxygen stored?
14. How does the industrial production of oxygen by electrolysis differ from the details of the laboratory preparation by electrolysis?

**b. Catalysis (33).**

15. Define and illustrate catalyst, catalysis, enzyme, hormone, inhibitor.

## IV. Atomic and physical properties of oxygen (34).

16. State some of the physical properties of oxygen in the gaseous, liquid and solid state.
17. What is meant by critical temperature? Critical pressure? Illustrate in the case of oxygen.
✓ 18. Fish live upon the oxygen in the sea. Are they able to split water into its constituent elements?

## V. Chemical properties of oxygen.

### Oxygen with non-metals, metals, and hydrogen (35).

19. Name 3 metals and 3 non-metals which will burn in oxygen; and the products of the combustion. What is formed when these oxides are dissolved in water?
20. Which metals and which non-metals do not combine directly with oxygen?

## VI. Some oxidations (36).

### a. Rusting of metals (37).

21. Why does grease or stove-polish rubbed upon an iron stove prevent it from rusting?

### b. Biological oxidations (38).

22. Describe the action of the red blood corpuscles.
23. State some of the medical uses of oxygen.

### c. Combustion of fuels (39).

24. What compounds are generally formed when fuels burn in air?
25. Define some units of heat. What is a B.T.U.?
26. What is the greatest use for industrial oxygen?

### d. Spontaneous combustion (40).

27. Explain why a hay-stack burns spontaneously.
28. Why should there be no danger of a pile of steel wool burning spontaneously?

### e. Dust explosions. Speed of oxidation (41).

29. Explain why dust in a flour mill explodes.
30. Name and illustrate 4 factors which speed up oxidation.
31. Define and illustrate dust explosion, kindling temperature, spontaneous combustion, calorie, heat of combustion, catalyst, oxidizing agent, exothermic reaction.
32. A draft increases combustion. Why? How is it possible, then, to blow out a candle?

## VII. Oxidizing Agents (42).

33. Define "oxidizing agent." Name three.

# CHAPTER V

# HYDROGEN

**43. History of Hydrogen.**—Paracelsus (1493–1541) knew that iron and sulfuric acid interact to form a gas. He said that when the acid and iron interact, "an air arises which bursts forth like the wind." Cavendish first ascertained the true nature of the gas in 1766, and he called it "inflammable air." In 1781 he proved that hydrogen burns in air to form nothing but water. Lavoisier (1783) named the gas **hydrogen** (Greek, meaning *water-producer*).

**44. Occurrence of Hydrogen.**—Hydrogen occurs in the free state in certain volcanic emanations; it is present in the intestinal gases of many animals; the gas is present in the natural gas of Ohio and Indiana: less than 0.000,005 per cent is present in the atmosphere; it is found in the carnallite of the Stassfurt potash mines and in certain meteorites; the spectroscope shows that hydrogen is present in the sun, many stars, and nebulae. The chromosphere of the sun owes its name to the fact that as seen momentarily, during a total eclipse, it is of a bright scarlet caused by glowing hydrogen. Huge red streamers sometimes extend 500,000 miles from the sun's disc (Fig. 18).

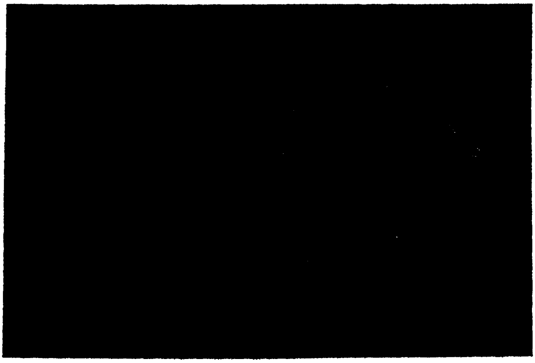


FIG. 18. Corona streamers. *Photographed by Paul A. McNally, Georgetown College Observatory, August 31, 1932. From Baker's Astronomy.*

In the combined state hydrogen occurs extensively. Water contains 11.19 per cent of hydrogen; it is an essential constituent of all acids, hydrocarbons, and vegetable and animal matter; it is also a constituent of very many of the carbon compounds, such as the alcohols, ethers, sugars, starch, and cellulose.

**45. Preparation of Hydrogen. Order of Activity of the Metals. —In the laboratory, hydrogen is prepared chiefly from the reaction of an acid with zinc; and in the research laboratory by electrolysis using iron or nickel electrodes, or by the purification of industrial hydrogen. In industry there are at least five major sources of cheap hydrogen.**

Underlying these preparation methods is the concept of the relative activities of the metals. In section 25 we learned that iron displaced copper from a solution of copper sulfate. If this is any criterion, iron must be more active than copper. In the same section we saw that mercury displaces silver, and zinc displaces lead, which, by this same criterion, indicates that mercury is more active than silver; zinc, more active than lead. This relative activity of different metals can also be measured by electrical methods. As a result the metals may be arranged in a series in which each element is more active than the elements below it. Such a table for some common metals follows on page 66, together with interesting relationships within the series. This table will be referred to repeatedly in discussing the preparation of hydrogen.

### 46. Laboratory Methods for Preparing Hydrogen.—

**a. From Water plus a Metal.**

**(1) Cold water with an active metal (alkali metal or alkaline earth metal).**

#### DEMONSTRATION 19. PREPARATION OF HYDROGEN FROM SODIUM AND WATER

Materials: Sodium kept under kerosene, forceps, knife, beaker of water, red litmus paper, test-tube, splinter.

A piece of **sodium,** freshly cut in order to demonstrate its metallic lustre, is thrown upon water. (*Care!*) Hydrogen is liberated, accompanied by a hissing sound and the evolution of heat. The solution of sodium hydroxide which forms is alkaline, for it is soapy to the touch and turns red litmus blue. The

Henry Cavendish (1731–1810)

Characterized by his biographer as "the wisest of the rich, and the richest of the wise," a man of wealth and high social position, he lived a recluse, devoting his time largely to research. He established the elementary nature of hydrogen and the composition of water; he synthesized nitric acid.

TABLE 9. ORDER OF ACTIVITY OF METALS

<table>
<tr><th></th><th></th><th>liberate $H_2$ from cold water</th><th>liberate $H_2$ from steam</th><th>liberate $H_2$ from acids</th><th>add $O_2$ at 20°</th><th>add $O_2$ on heating</th><th>oxides lose $O_2$ on heating</th><th>oxides heated with $H_2$ reduce to free metal</th><th>occur free in nature</th></tr>
<tr><td rowspan="2">alkali metals</td><td>Potassium</td><td rowspan="3">liberate $H_2$ from cold water</td><td></td><td rowspan="11">liberate $H_2$ from acids</td><td rowspan="2">add $O_2$ at 20°</td><td></td><td></td><td></td><td></td></tr>
<tr><td>Sodium</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td rowspan="2">alkaline earth metals</td><td>Calcium</td><td rowspan="6">liberate $H_2$ from steam</td><td></td><td rowspan="12">add $O_2$ on heating</td><td></td><td></td><td></td></tr>
<tr><td>Magnesium</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td>Aluminum</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td>Manganese</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td>Zinc</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td>Iron</td><td></td><td></td><td></td><td rowspan="10">oxides heated with $H_2$ reduce to free metal</td><td></td></tr>
<tr><td></td><td>Nickel</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td>Tin</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td>Lead</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td><b>Hydrogen</b></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td>Copper</td><td></td><td></td><td></td><td></td><td></td><td rowspan="5">occur free in nature</td></tr>
<tr><td></td><td>Mercury</td><td></td><td></td><td></td><td></td><td rowspan="4">oxides lose $O_2$ on heating</td></tr>
<tr><td rowspan="3">noble metals</td><td>Silver</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Platinum</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Gold</td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

equation for the reaction is as follows:

$$\underset{\text{Sodium}}{2Na} + 2H_2O \rightarrow \underset{\text{Sodium hydroxide}}{2NaOH} + H_2\uparrow .$$

By introducing a small piece of sodium (*Care!*) into a test-tube filled with, and inverted over, water, hydrogen may be collected and tested with a glowing splint.

Potassium is more active than sodium; and reacts so violently with cold water that the escaping hydrogen ignites spontaneously, burning with a violet flame due to the vapor of potassium. Calcium and magnesium are much less active.

(2) **Steam with a less active metal,** such as magnesium, liberates hydrogen:

$$Mg + H_2O \rightarrow MgO + H_2 \uparrow .$$

The metal burns (oxidizes) producing light, and water is reduced. MgO is formed instead of $Mg(OH)_2$, for all common hydroxides, except NaOH and KOH, are decomposed at high temperatures: *e.g.*, $Mg(OH)_2 \rightleftarrows MgO + H_2O$.

In the same way all of the metals above hydrogen in the activity series, table 9, displace hydrogen from steam. Hydrogen is not liberated by copper and the metals below it in the series.

### b. From Dilute Acids plus a Metal.

Dilute acids are attacked by active and moderately active metals such as Mg, Zn, Fe and Al. We say that the metal **displaces** hydrogen from the acid. The metals below hydrogen in the activity series (Cu, Hg, Ag, Au, Pt) do not displace hydrogen from acids.

Zinc and iron are most commonly employed, although magnesium is more active. Hydrochloric or sulfuric acid are the acids generally used; nitric acid is unsuitable since it is an active oxidizing agent.

### • DEMONSTRATION 20. PREPARATION OF HYDROGEN FROM ZINC AND ACID

Materials: Set-up as in Fig. 19; 150 cc. bottle, granulated zinc, concentrated hydrochloric acid, 3 test-tubes, cupric chloride solution.

The concentrated hydrochloric acid runs down the thistle tube and becomes diluted with water; and then reacts with the granuated zinc, liberating hydrogen. The addition of a few cc. of cupric chloride or cobalt chloride catalyzes the reaction, by forming an electric couple. Commercial granulated zinc contains such catalytic impurities and for this reason reacts much faster than pure zinc with the dilute acid. The hydrogen thus formed contains traces of impurities which may be removed by passing the gas through certain solutions. For preparing large quantities in the laboratory, a **Kipp generator** (Fig. 19) is very convenient. It is easy to regulate the supply of gas, for when the stopcock is closed the gas accumulates in the middle globe, which forces out the acid.

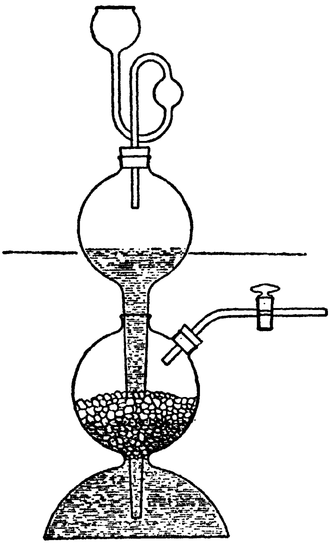


FIG. 19. A Kipp generator. How does it work?

The following are typical equations, showing the preparation of hydrogen from the action of a metal upon dilute acids:

$$Fe + H_2SO_4 \rightarrow \underset{\text{Ferrous sulfate}}{FeSO_4} + H_2\uparrow .$$

$$Zn + H_2SO_4 \rightarrow \underset{\text{Zinc sulfate}}{ZnSO_4} + H_2\uparrow .$$

$$2Al + 6HCl \rightarrow \underset{\text{Aluminum chloride}}{2AlCl_3} + 3H_2\uparrow .$$

Note that *diluted acids must be used.* To illustrate, if zinc be dissolved in concentrated sulfuric acid, the acid suffers reduction (loses oxygen), hydrogen sulfide ($H_2S$) being formed:

$$4Zn + 5H_2SO_4 \rightarrow 4ZnSO_4 + 4H_2O + H_2S.$$

Sulfur and sulfur dioxide may also be formed, since they are reduction products of $H_2SO_4$.

**c. From Hydroxides plus a Metal.**

Hydrogen can be prepared by treating certain metals with hydroxides. Thus aluminum turnings may be boiled with a solution of sodium hydroxide:

$$2Al + 2NaOH + 2H_2O \rightarrow 3H_2 + \underset{\text{sodium aluminate}}{2NaAlO_2};$$

or zinc and solid sodium hydroxide may be heated:

$$Zn + 2NaOH \rightarrow H_2 + \underset{\text{sodium zincate}}{Na_2ZnO_2}.$$

A method for preparing hydrogen, known as the **silicol process**, is based upon heating powdered silicon, or an alloy of silicon and iron (*ferrosilicon*), with a concentrated solution of sodium hydroxide:

$$Si + 2NaOH + H_2O \rightarrow 2H_2 + \underset{\text{sodium silicate}}{Na_2SiO_3}.$$

The filling of military balloons with hydrogen was once greatly facilitated by this reaction. For every 1,000 cubic feet of hydrogen 275 pounds of sulfuric acid and 157 pounds of iron; but only 58 pounds of ferrosilicon and 125 pounds of sodium hydroxide are required. Hydrogenite, a mixture of ferrosilicon and sodium hydroxide, has also been used.

### d. By Electrolysis.

This method has already been discussed under the preparation of oxygen, section 32, *d*. Oxygen is given off at the positive pole, or **anode**; hydrogen is given off at the negative pole, or **cathode.** See also Demonstration 13, section 32, *d*.

**47. Industrial Methods for Preparing Hydrogen.**—Large quantities of hydrogen are required in our factories today. Each manufacturer utilizes the method most suited to his needs as regards purity, availability of raw materials, outlet for by-products formed in the process and so forth.

### a. From Water Gas.

(1) Water gas is first manufactured by passing steam over coke (carbon) at 1,000° C.:

$$C + H_2O \rightarrow H_2 + CO.$$

By producing a low temperature and applying pressure, the carbon monoxide liquefies, leaving the hydrogen as a gas.

(2) Water gas is manufactured as above, and the hydrogen and carbon monoxide, along with an excess of steam, are passed over a catalytic mixture of oxides of iron, chromium, and thorium at 500°. CO is oxidized to $CO_2$:

$$CO + H_2O \rightleftarrows CO_2 + H_2.$$

The carbon dioxide is then removed, leaving the hydrogen.

### b. By the Electrolysis of Water.

This process is carried out on a large scale using iron tanks containing sodium hydroxide dissolved in water to make it a conductor. In 1928 Noeggerath proposed a saving of electricity by carrying out the electrolysis at high pressures, 200 atmospheres.

### c. From Ammonia.

In this process, the manufacturer combines hydrogen, as water gas, with nitrogen to form ammonia:

$$3H_2 + N_2 \xrightarrow[\text{200 atmos. or more}]{\text{Fe } 500^\circ} \underset{\text{ammonia}}{2NH_3}.$$

The ammonia is liquefied and shipped to some chemical firm. The latter passes the ammonia over an iron catalyst at 500° C.

and recovers the hydrogen:

$$2NH_3 \xrightarrow[\text{1 atmos.}]{\text{Fe}\ 500^\circ} N_2 + 3H_2.$$

Strangely enough, the manufacturer can sell hydrogen in this round-about fashion at a lower figure than he can sell hydrogen alone. The reason lies in the lower shipping charges for liquid ammonia in tank cars than for compressed hydrogen in heavy steel tanks.

It will be noticed that the two reactions above are just the reverse of one another. Such reactions are called **reversible reactions.** We shall have more to say about them in Section 48.

### d. By the Electrolysis of Brine.

During the electrolysis of a water solution of common salt (NaCl), in the commercial production of chlorine and sodium hydroxide, hydrogen is given off as a by-product:

$$2NaCl + 2H_2O \xrightarrow[\text{electrolysis}]{} 2NaOH + Cl_2\uparrow + H_2\uparrow.$$

### e. By Cracking Hydrocarbons.

Hydrogen is formed when mineral oils and natural gas (compounds of hydrogen and carbon) are "cracked" or broken down by heat. Coke-oven gas contains free hydrogen.

### f. By Iron Contact Processes.

(1) In the **Lane Process,** steam is first passed over red-hot iron:

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2.$$

In the course of time the reaction stops, owing to the formation of a protecting film of oxide. **Water gas** (hydrogen + carbon monoxide, formed by passing steam over red-hot coke) is then turned on, which reduces $Fe_3O_4$ to iron. Water gas is then shut off and more steam turned on. By the alternate use of steam and water gas, a small quantity of iron can be used almost indefinitely.

(2) In the **Bergius Process,** iron and water are heated in a bomb to 300° under a pressure of 100 atmospheres:

$$Fe + H_2O \rightleftarrows FeO + H_2.$$

**48. Reversible Reactions.**—We have just seen that at 500° C. nitrogen and hydrogen combine to form ammonia if the pressure is 200 atmospheres; but that ammonia dissociates into nitrogen and hydrogen at 1 atmosphere pressure. In the same way, section 32, mercuric oxide may be decomposed into mercury and oxygen at one temperature; but at a lower temperature, oxygen and mercury recombine to form mercuric oxide. In other words, these are reversible or opposed actions.

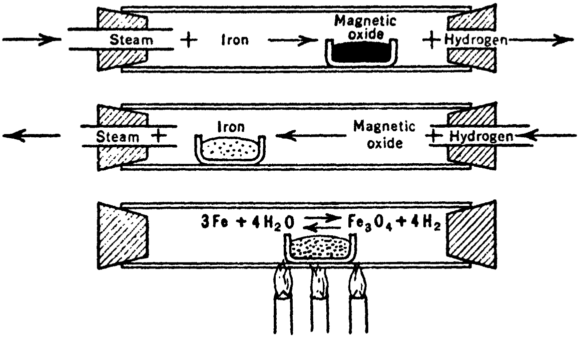


FIG. 20. A reversible reaction.

By choosing suitable conditions, many chemical reactions may be made to proceed in either direction. Thus, when steam is passed over red-hot iron, the chemical change may be represented as follows:

$$3Fe + 4H_2O \rightarrow 4H_2 + \underset{\text{magnetic oxide}}{Fe_3O_4} \quad (1).$$

When hydrogen is passed over heated magnetic oxide of iron we have:

$$Fe_3O_4 + 4H_2 \rightarrow 4H_2O + 3Fe \quad (2).$$

Equation (2) is just the reverse of equation (1). In order to complete the reaction represented by (1), an excess of steam is employed, the hydrogen being allowed to escape (Fig. 20). The reverse action (2) may be completed by passing a large excess of hydrogen over the hot oxide of iron, the steam being removed or condensed.

If, however, we heat either pair of substances—iron and steam or oxide of iron and hydrogen—in a closed vessel, the action cannot be completed in either direction; for the two actions oppose each other:

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2 \quad (3).$$

Under these conditions we do not end up with either pair but with a mixture of all four substances. For any given set of conditions (*e.g.*, 440° C. and 1 atmosphere) the ratio of the amounts of these four substances will always be the same, irrespective of what we started the experiment with. This is called the **state of equilibrium.** After reaction has proceeded to this given ratio there will be no further change in the relative quantities of the reacting substances, since the reaction to the right will just balance the speed of the action to the left, Fig. 20.

**49. Atomic and Physical Properties of Hydrogen.**—Hydrogen is a colorless, odorless, and tasteless gas. It is 14.4 times lighter than air.

TABLE 10. ATOMIC AND PHYSICAL PROPERTIES OF HYDROGEN

| | | | |
|---|---|---|---|
| Symbol | H | $d_{gas}$ | 0.00008985 |
| At. wt. | 1.0080 | $d_{liq}$ | 0.071 |
| At. no. | 1 | B.P. | −252.7° C. |
| Electrons | 1S′ | M.P. | −259.2° C. |
| Isotopes and relative abundance | 1....6900 parts<br>2....1 part<br>3....trace | C.T. | −241° C. |
| | | C.P. | 20 atmos. |
| | | Solubility in 100 cc. water | 1.93 cc. at 0° C. |

DEMONSTRATION 21. HYDROGEN LIGHTER THAN AIR

Materials: Two test-tubes, one filled with hydrogen; splinter, large inverted beaker or flask suspended from one arm of a balance which has been carefully counterpoised, soapy water, tank hydrogen, soap bubble pipe.

Hydrogen is the lightest known gas; its extreme lightness may be demonstrated by pouring the gas upward into a test-tube; by allowing it to flow into an inverted beaker on a balance; and by blowing soap bubbles with the gas.

Liquid hydrogen is colorless; upon evaporating rapidly it freezes into a white solid (Travers). All other known gases, except helium, solidify easily when led into a vessel surrounded by liquid hydrogen.

Hydrogen is absorbed by many metals. Graham proposed the name **occlusion** (Latin, *occludo,* I shut up) for this phenomenon. Palladium, platinum, gold, iron, nickel, and cobalt are among the metals which absorb the gas. Palladium black at ordinary temperatures absorbs between 800 and 900 volumes of hydrogen; platinum in fine powder absorbs about 50 volumes; iron, 19; and silver, none.

When hydrogen is allowed to impinge upon finely divided platinum exposed to the air, so much heat is generated by the absorption of the gas and the hydrogen becomes so active that it ignites. This is the principle involved in the construction of the **Döbereiner lamp** and certain automatic cigar lighters.

Hydrogen diffuses more rapidly than any other gas.

**50. Chemical Properties of Hydrogen.**—Hydrogen does not unite with as many elements as does oxygen.

### a. Hydrogen and Oxygen.

These two gases at 180° C. combine only slowly; above 550° C. they explode to form water:

$$\begin{array}{ccccc} 2H_2 & + & O_2 & \rightarrow & 2H_2O. \\ (2 \times 2.016 \text{ g.}) & + & (2 \times 16 \text{ g.}) & = & (2 \times 18.016 \text{ g.}) \end{array}$$

That water is the product of combustion may be shown by allowing a jet of burning hydrogen to impinge upon a glass vessel containing cold water. The gas is dried before burning by passing it through a tube containing calcium chloride.

When hydrogen burns, a large quantity of heat is liberated (exothermic reaction). This fact is utilized in the oxyhydrogen blowpipe invented by Robert Hare of Philadelphia in 1801. So intense is the heat generated that platinum may be readily melted; and a steel spring or wire burns in it brilliantly. In a closed space the temperature may rise to over 2,500° C.

The oxyacetylene blowpipe or torch has partially displaced the oxyhydrogen blowpipe. Acetylene gas ($C_2H_2$) is substituted for hydrogen, and the temperature obtained is higher (about 3,300° C.). As this flame will not oxidize metals, it is very suitable for welding materials.

### b. Hydrogen and Non-metals.

Hydrogen combines directly with the halogens. Thus a mixture of hydrogen and chlorine will explode when heated, or when exposed to intense light:

$$H_2 + Cl_2 \rightarrow 2HCl.$$

We have already seen that hydrogen combines directly with *nitrogen at high pressures over a catalyst to form ammonia* (Section 47, *c*). Also, hydrogen unites directly with sulfur to form hydrogen sulfide ($H_2S$).

### c. Hydrogen and Metals.

Hydrogen combines directly with the more active metals to form hydrides, *e.g.*, NaH, sodium hydride; CaH, calcium hydride.

### d. Hydrogen as a Reducing Agent. Oxidation and Reduction.

In section 36 we learned that the addition of oxygen to a substance is called **oxidation.** The converse of this is known as **reduction.** Oxidation always accompanies reduction. Thus in the reactions

$$CuO + H_2 \rightarrow Cu + H_2O,$$
$$Fe_3O_4 + 4H_2 \rightleftarrows 3Fe + 4H_2O,$$

while hydrogen is *oxidized* to water, the copper oxide and the iron oxide are *reduced* to copper and iron.

Hydrogen is a powerful **reducing agent;** it reduces the heated oxides of many of the metals; also some of the compounds of chlorine. Hydrogen occluded by palladium is especially active as a reducing agent, readily reducing ferric salts to ferrous salts, nitrates to nitrites and ammonia, and chlorates to chlorides, etc.

DEMONSTRATION 22. HYDROGEN REDUCING COPPER OXIDE

**Materials:** Kipp generator for hydrogen, copper oxide, porcelain boat fitting inside a hard glass tube 2′ long and clamped over a burner with wing tip.

The reducing action of hydrogen can be shown by passing it over the heated copper oxide. Red copper is left in the boat, and water condenses upon the cooler part of the tube.

### e. Atomic Hydrogen.

When hydrogen molecules are passed through an electric spark, they are dissociated into atoms:

$$\underset{\text{molecule}}{H_2} + \underset{\text{(104,000 cals.)}}{\text{energy}} \rightarrow \underset{\text{atomic hydrogen}}{H + H.}$$

These atoms are extremely short-lived, recombining to form molecules under ordinary conditions in less than a millionth of a second. Yet, because of the tremendous number of collisions which molecules suffer with one another, they may undergo many interesting reactions during their brief life span. Since 1920 H. S. Taylor at Princeton, Bohnoeffer and Polanyi formerly in Berlin, and other physical chemists have busied themselves with problems involving the reactions of these hydrogen atoms.

Hydrogen atoms are also formed when molecules of hydrogen collide with mercury atoms which have been "excited" by a radiation emitted by a cooled mercury arc. Hydrogen thus formed is exceedingly active. For instance, it will reduce metallic oxides at room temperature, react with oxygen to form hydrogen peroxide and water, and with carbon monoxide to form formaldehyde ($CH_2O$).

**51. Uses of Hydrogen.**—In recent years the use of hydrogen on an industrial scale has increased enormously.

During the World War of 1914–18 quantities were used for **inflating airships.** With the tragic explosion of the Hindenburg

*Coyprigh by International News Photo*

FIG. 21. The explosion of the Hindenburg.
$2H_2 + O_2 \rightarrow 2H_2O$.

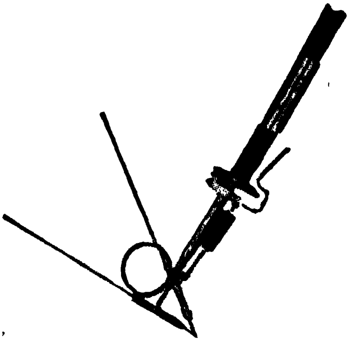
at Lakehurst, New Jersey, in 1936 (Fig. 21), the popularity of Zeppelins rapidly dwindled. Wherever helium is available a non-inflammable mixture containing about 15 per cent helium and 85 per cent hydrogen is substituted.

After 1912, following the researches of Sabatier on the **catalytic hydrogenation of oil,** a huge quantity of hydrogen was demanded by the edible oil industries. When certain oils, *e.g.*, cottonseed oil, are treated with hydrogen in the presence of such catalysts as nickel and nickel oxide, the unsaturated oil (liquid fat) combines with the gas to form a solid fat: *e.g.*, large quantities of "Crisco" and other substitutes for lard are manufactured by hydrogenation. This process is adding enormously to the value of our cottonseed oil; and the amount of solid fat produced annually is equal to that obtained from 7,000,000 hogs. About 300,000,000 pounds of oils are hydrogenated annually in the United States. Due to hydrogenation, there is a greatly expanded whaling industry in Arctic and Antarctic seas. An amusing commentary on the rôle of chemistry in our economic world today has been the remark that one way to solve the cotton problem of the Southern States is to raise poorer cotton with larger seeds; and profits will come from the hydrogenated cottonseed industry, rather than from the cotton.

A host of processes developed during the active period of chemical industry from 1925 to 1940 employ water gas as a raw material. These include the manufacture of wood alcohol and gasoline from coal, and the hydrogenation of poor grade petroleum to a good quality gasoline. The hydrogenation of nitrogen at high pressures to form ammonia, from which explosives were made, enabled Germany to continue the first World War.

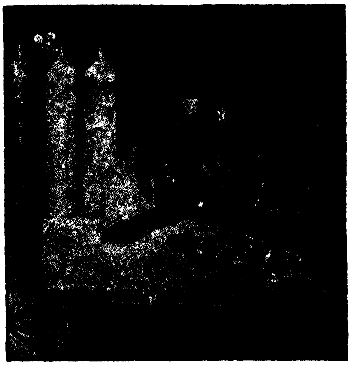
Not the least interesting industrial use of hydrogen has been the **atomic hydrogen gun,** invented by Irving Langmuir, Nobel Prizeman in Chemistry for 1934, of the General Electric Company. In this apparatus (Fig. 22) a stream of hydrogen molecules are split into atoms by an electric spark. A short distance further on, the atoms recombine (that is, the reaction $H_2 + 104{,}000 \text{ cals.} \rightarrow H + H$ is reversible), and the 104,000 cals., per 2.016 grams of hydrogen, can be concentrated at a point. By means of this device extremely high temperatures may be realized, even higher than the oxyacetylene flame, which is of great value in welding metals. Minute flames of atomic hydrogen can be produced and maintained, thus making it possible to weld sheets of metal as thin as five one-thousandths of an inch (Fig. 23).

According to Langmuir, iron can be melted in the flame of atomic hydrogen without contamination by carbon, oxygen, or nitrogen. As atomic hydrogen has reducing action, alloys containing chromium, aluminum, silicon, or manganese can be melted without fluxes and without surface oxidation.



*Courtesy of the General Electric Company.*

FIG. 22. The Langmuir hydrogen atom torch.
$H + H \rightarrow H_2 + 104{,}000$ cals.



*Courtesy of the Hughes Tool Company.*

FIG. 23. Atomic hydrogen welder building hard surface on a bit.

**52. Heavy Hydrogen.**—In 1931 Urey and Washburn showed that ordinary hydrogen always contains a trace of another kind of hydrogen atom which is twice as heavy (atomic weight 2.00147). This has been called **heavy hydrogen** or **deuterium** (symbol **D**). The ratio of light to heavy hydrogen in all naturally occurring compounds containing hydrogen is always the same. This ratio has been established as H : D :: 6900 : 1 by Dole from a careful analysis of Lake Michigan water.

To obtain a pure sample of heavy hydrogen several methods have been employed, and will be described in detail later. The first successful method was by repeated electrolysis of water, using nickel-iron electrodes. Heavy water is not as readily split by the electric current as is light water. Hence the off-gas is richer in light hydrogen, and the deuterium is concentrated about 6-fold in the residue. Since the electrolysis must be continued for a long period, involving a costly expenditure of electricity, advantage is gained by commencing with a sodium hydroxide solution removed from the bottoms of commercial electrolytic tanks (32, *d*) where electrolysis has already been in progress for several years.

The chemical properties of heavy and light hydrogen differ in some slight respects, which will be described later (243). The physical properties of deuterium also differ somewhat from ordinary hydrogen. Thus it liquefies at −249.5° C. instead of at −252.7° C.; it solidifies at −254.3° C., instead of at −259.2° C.

**53. Ortho and Para Hydrogen.**—In 1929 K. F. Bonhoeffer in Berlin, Germany, showed that the two atoms of a hydrogen molecule, $H_2$, could unite in two different ways. This gave rise to two types of hydrogen molecules, named **ortho** and **parahydrogen**. In the former it is assumed that the nuclei of the two atoms are spinning in the same direction; in parahydrogen they are spinning in opposite directions. For the present the student will find interest in the fact that the existence of these two types of hydrogen molecules was predicted by the mathematicians long before Bonhoeffer went into the laboratory and discovered them.

The percentage of parahydrogen falls steadily as temperature is increased. Thus it is 99.7 per cent at the temperature of liquid hydrogen, 50 per cent at liquid air temperatures, and only 25 per cent at room temperature. Bonhoeffer discovered that if a 25–75 mixture of para-ortho was passed into a charcoal catalyst at liquid air temperatures, it changed rapidly into the proper 50–50 mixture. He followed this change by measuring specific heats and demonstrated it for the first time at the Minneapolis meeting of the American Chemical Society in 1929.

**Reading References:** Articles number 8, 403, 408, 410, 414 and 423 in the Appendix.

## QUESTION REVIEW

I. HISTORY OF HYDROGEN (43).

1. During what period in chemical history was a gas obtained from acid plus metal? What did Cavendish discover? What does the word *hydrogen* mean?

II. OCCURRENCE OF HYDROGEN (44).

2. Name 4 places where hydrogen occurs in the free state.

III. PREPARATION OF HYDROGEN.

**a. Order of activity of metals (45).**

3. What experiment can you describe which shows that one element is more active than some other one?
4. Arrange the following elements in order of their chemical activity: mercury, magnesium, calcium, gold, iron, hydrogen, copper, zinc, potassium, platinum, and sodium.
5. Draw a chart illustrating the chemical reactions of the metals.

**b. Laboratory methods for preparing hydrogen: (1) water plus metal, (2) dilute acid plus metal, (3) hydroxides plus metal, (4) electrolysis (46).**

6. Illustrate with one example each the 4 methods listed above for the laboratory preparation of hydrogen.

**c. Industrial methods for preparing hydrogen: (1) from water-gas, (2) by electrolysis of water, (3) from ammonia, (4) by electrolysis of brine, (5) by cracking hydrocarbons, (6) by iron contact processes (47).**

7. Illustrate each of the above 6 methods for the industrial preparation of hydrogen.
8. Why is hydrogen from ammonia cheaper than the original hydrogen from which the ammonia was made?
9. What conditions of temperature and pressure favor the formation of ammonia? What causes its decomposition? What conditions favor the formation of FeO rather than $Fe_3O_4$ from the action of steam on iron?
10. Name several common metals which will decompose water. Several metals which will not decompose water.

**d. Reversible reactions (48).**

11. How would you prove experimentally that the action of steam upon heated iron is reversible? What is meant by a state of chemical equilibrium?

IV. Atomic and physical properties of hydrogen (49).

12. Mention a few physical properties of hydrogen.
13. Explain why finely divided platinum will cause a mixture of hydrogen and oxygen to explode.
14. Define and illustrate *occlusion*.

V. Chemical properties of hydrogen (50).

15. Who invented the oxyhydrogen blowpipe? Why is the oxyacetylene torch often better?
16. With what non-metals does hydrogen combine directly?
17. What general name is given to the compounds hydrogen forms with metals? Give an example.
18. Show by means of equations that hydrogen is a reducing agent. Indicate whether oxidation has occurred.
19. How are hydrogen atoms produced? How long do they stay as monatomic particles? State one chemical reaction which takes place with hydrogen atoms.

VI. Uses of hydrogen (51).

20. What future is there for Zeppelins, from a chemical standpoint?
21. What important foods are the product of hydrogenation?
22. Mention some synthetic materials which employ water gas as raw material.
23. Why would the first World War have quickly terminated if large supplies of hydrogen had not been available?
24. Describe the atomic hydrogen gun. Who invented it? What advantages has it over the oxyacetylene flame?

VII. Heavy hydrogen (52).

VIII. Ortho and para hydrogen (53).

# CHAPTER VI

## PRACTICE IN CHEMICAL SHORTHAND

**54. Symbols and Valence.**—Having now acquired a familiarity with a considerable number of chemical compounds and their reactions, we shall return to an intensive practice in the writing of chemical formulas and equations. To this end, the student should memorize Tables 6 and 7 which give the symbols and valences of a number of chemical elements. Also, the exercises at the end of this chapter should be thoroughly mastered.

**55. Experimental Evidence for Valence.**—On a number of occasions certain valences have been dogmatically stated. Why is aluminum +3 and sodium +1? What evidence is there for the values so assigned? How have these been determined experimentally? In answer to these questions, three different lines of evidence will be presented.

### a. Electrical Evidence of Valence.

We have already learned that water is electrolyzed into hydrogen and oxygen. In the same way when electricity is passed through certain solutions containing compounds of metals like sodium, magnesium, copper, or aluminum, these metals will deposit out. This is the principle of electroplating. Now electricity is the flow of negatively charged particles, called **electrons**; and it is possible to measure the *number of electrons* flowing per second in a given current. Also, the weight of metal deposited by this current divided by the weight of one atom of the metal gives the *number of atoms* deposited per second. Comparing these two values it is found that

to deposit 1 atom of sodium (Na) requires 1 electron
to deposit 1 atom of magnesium (Mg) requires 2 electrons
to deposit 1 atom of copper (Cu) requires 2 electrons
to deposit 1 atom of aluminum (Al) requires 3 electrons.

For many reasons which will be presented later, it is thought that the metals are present in solution not as *atoms* but as charged particles called **ions**; and that the action of the electric current is to neutralize these charged particles according to the scheme

$$\begin{array}{rcccl}
\mathrm{Na^{+1}} & + & 1e & \rightarrow & \mathrm{Na^{0}} \\
\mathrm{Mg^{+2}} & + & 2e & \rightarrow & \mathrm{Mg^{0}} \\
\mathrm{Cu^{+2}} & + & 2e & \rightarrow & \mathrm{Cu^{0}} \\
\mathrm{Al^{+3}} & + & 3e & \rightarrow & \mathrm{Al^{0}}. \\
\text{(ions)} & & (-) & & \text{(atoms)}
\end{array}$$

The charges on these ions correspond to the valences of the metals.

**b. Chemical Determination of Valence.**

In the preparation of hydrogen from acids (46b), it was shown that atoms of different elements displace a definite number of hydrogen atoms. This fact may be illustrated by the following equations where 1Na gives 1H, 1 Mg gives 2H, and 1Al gives 3H.

$$\begin{array}{lcccccccccl}
(1) & \mathrm{Na} & + & \mathrm{HCl} & \rightarrow & \mathrm{NaCl} & + & \mathrm{(H)} & & & \\
& 23\text{ g.} & & 36.468\text{ g.} & & 58.46\text{ g.} & & 1.008\text{ g.} & \rightarrow & 11.2\text{ liters} \\
& & & & & & & & & \text{at S.T.P.} \\
(2) & \mathrm{Mg} & + & \mathrm{2HCl} & \rightarrow & \mathrm{MgCl_2} & + & \mathrm{(2H)} & & & \\
& 24.32\text{ g.} & & 2 \times 36.468\text{ g.} & & 95.24\text{ g.} & & 2 \times 1.008\text{ g.} & \rightarrow & 22.4\text{ liters} \\
& & & & & & & & & \text{at S.T.P.} \\
(3) & \mathrm{Al} & + & \mathrm{3HCl} & \rightarrow & \mathrm{AlCl_3} & + & \mathrm{(3H)} & & & \\
& 27\text{ g.} & & 3 \times 36.468\text{ g.} & & 133.38\text{ g.} & & 3 \times 1.008\text{ g.} & \rightarrow & 33.6\text{ liters} \\
& & & & & & & & & \text{at S.T.P.}
\end{array}$$

### DEMONSTRATION 23. DISPLACEMENT OF HYDROGEN AS A MEASURE OF VALENCE

**Materials:** 30 cm. crystallizing dish half full of dilute hydrochloric acid; 3 50-cc. test-tubes; 3 small funnels; 3 watch glasses containing 23 mg. of sodium (under kerosene), 24 mg. of magnesium, and 27 mg. of aluminum respectively.

W. A. Noyes describes an instructive experiment illustrating this point: "If 23 milligrams of sodium, 24 milligrams of magnesium, and 27 milligrams of aluminum are allowed to act on hydrochloric acid in such a way that the hydrogen is generated in separate tubes, it will be found that the sodium will give about 11 cc. of hydrogen, the magnesium 22 cc., and the aluminum 33 cc." (Fig. 24.) The ratios 23 : 24 : 27 and 11 : 22 : 33 are roughly the same as in the foregoing equations, and accordingly confirm the formulas $\mathrm{Na^{+1}Cl}$, $\mathrm{Mg^{+2}Cl_2}$, and $\mathrm{Al^{+3}Cl_3}$.

From the above evidence we may generalize as a chemical method for determining the valence of metals: **the valence of a metal is equal to the number of hydrogen atoms liberated from acids by one atom of the metal.**

For non-metals another device is employed. When the formulas of compounds of hydrogen with non-metals are determined, it is found that non-metals differ as regards the number of hydrogen atoms held in combination. To illustrate:

| $HCl$ | $H_2O$ | $NH_3$ | $CH_4$ |
|---|---|---|---|
| hydrogen chloride | water | ammonia | methane |

It is clear from these formulas that non-metals may differ in their capacities for combining with hydrogen. From the formulas illustrated, we conclude that the valences of these particular non-metals are $Cl^{-1}$, $O^{-2}$, $N^{-3}$ and $C^{-4}$. To generalize: **the valence of a non-metal may be measured in terms of the number of hydrogen atoms uniting with one atom of the non-metal to form a compound.**

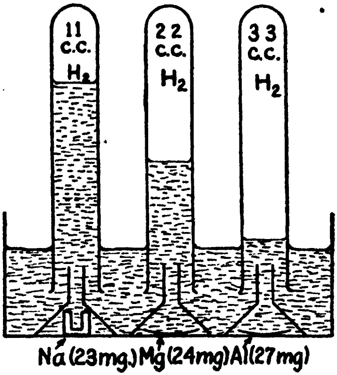


FIG. 24. Valence from displacement of hydrogen from acids.

**c. Atomic Structure Evidence of Valence.**

During this present century, the physicist and chemist have probed deep inside the atom. They now picture each atom as having a central sun with planets. The weight and positive charge of the atom is concentrated in the central sun. Electrons,

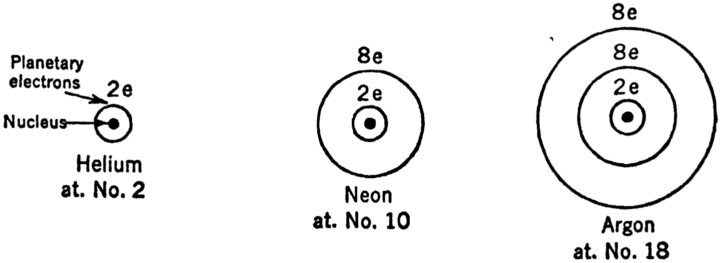


**FIG. 25. Arrangement of planetary electrons of some inert gases.**

negative particles of electricity, are the planets. We shall confine our remarks in this section solely to these **planetary electrons.** The number of planetary electrons possessed by each atom is given by its atomic number (286). This is the number in red in the table on the inside back cover of the text. By reference to this table it will be seen that hydrogen has only 1 planetary electron, sodium has 11, aluminum has 13, and so on. Now these electrons tend to arrange themselves in concentric shells (Fig. 25). For the first 18 elements in the table the arrangement is as follows.

TABLE 11. PLANETARY ARRANGEMENT OF ELEMENTS NUMBERS 1–18

| Atomic number | Element | Shell 1 | Shell 2 | Shell 3 |
|---|---|---|---|---|
| 1 | H | 1 | 0 | 0 |
| 2 | **Helium** | **2** | **0** | **0** |
| 3 | Li | 2 | 1 | 0 |
| 4 | Be | 2 | 2 | 0 |
| 5 | B | 2 | 3 | 0 |
| 6 | C | 2 | 4 | 0 |
| 7 | N | 2 | 5 | 0 |
| 8 | O | 2 | 6 | 0 |
| 9 | F | 2 | 7 | 0 |
| 10 | **Neon** | **2** | **8** | **0** |
| 11 | Na | 2 | 8 | 1 |
| 12 | Mg | 2 | 8 | 2 |
| 13 | Al | 2 | 8 | 3 |
| 14 | Si | 2 | 8 | 4 |
| 15 | P | 2 | 8 | 5 |
| 16 | S | 2 | 8 | 6 |
| 17 | Cl | 2 | 8 | 7 |
| 18 | **Argon** | **2** | **8** | **8** |

By interactions between these electrons, two or more atoms will combine to form a compound. An important generalization which is obeyed in forming these compounds is: **if atoms can come together in such a fashion that each atom assumes the planetary configuration of the nearest inert gas (helium 2–0–0; neon 2–8–0; argon 2–8–8; also 0) a stable compound will be formed.** For example: if sodium and chlorine are mixed, the sodium

(2–8–1) can lose one of its electrons to the chlorine (2–8–7) (Fig. 26). The sodium thereby becomes a sodium ion (2–8–0), similar in number to neon (2–8–0); while the chlorine, by gaining the electron from the sodium, becomes a chloride ion (2–8–8), similar to the argon configuration (2–8–8). This does not mean, however, that the chlorine and the sodium have taken on the properties of argon and neon; their nuclei are still nuclei of chlorine and of sodium. The sodium atom by losing one negative charge (one electron) becomes Na$^{+1}$, the chlorine gains an electron and becomes Cl$^{-1}$. The molecule which we have just formed is sodium chloride, NaCl; and we now have an inkling of why it consists of a sodium ion and a chloride ion; that is, Na$^{+1}$ Cl$^{-1}$. At the same time we have fixed the valences of sodium and of chlorine as $+1$ and $-1$.

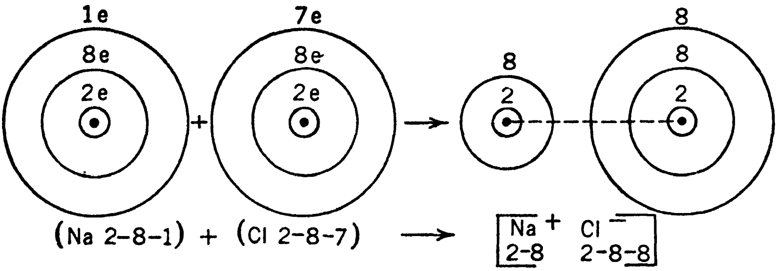


FIG. 26. A chemical combination in terms of planetary electrons.

To take another example, magnesium combines with chlorine to form the compound MgCl$_2$. Why, on the basis of atomic structure, should it require two atoms of chlorine to form a stable magnesium chloride molecule? The answer is: magnesium (2–8–2) loses two electrons, one to each chlorine atom (2–8–7). The magnesium thereby becomes 2–8–0, and the two chlorine atoms each become 2–8–8. Magnesium ions (Mg$^{+2}$) and chloride ions (Cl$^-$) are formed; the formula of the compound is MgCl$_2$; and the valences of magnesium and chlorine are $+2$ and $-1$ respectively.

Prediction of valences from a knowledge of atomic structure becomes considerably involved when the elements beyond argon are examined, particularly for elements of variable valence (Cu$^{+1}$ and Cu$^{+2}$).

**56. Valences of Some Compound Radicals.**—From Table 7 we learned the valences of a number of metals and non-metals.

When such elements occur in formulas they are often called **simple radicals.** Thus NaCl contains the sodium radical (Na) and the chloride radical (Cl). Groups such as $(SO_4)$ or $(NO_3)$ or $(ClO_3)$ are called **compound radicals.** These compound radicals frequently pass from compound to compound when chemical changes occur; they have, therefore, definite valences. Thus, the sulfate radical $(SO_4)$ has a valence of $-2$ for it is combined with two atoms of hydrogen in $H_2SO_4$. When sulfuric acid is treated with magnesium, hydrogen is evolved:

$$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2 \uparrow .$$

The valences and names of a number of important compound radicals follow, and should be memorized.

TABLE 12. VALENCES OF IMPORTANT COMPOUND RADICALS

| | | | |
|---|---|---|---|
| $(ClO_2)^{-1}$ chlorite | $(NO_2)^{-1}$ nitrite | $(SO_3)^{-2}$ sulfite | — |
| $(ClO_3)^{-1}$ chlorate | $(NO_3)^{-1}$ nitrate | $(SO_4)^{-2}$ sulfate | $(CO_3)^{-2}$ carbonate |

**57. Review and Extension of Nomenclature.**—The following rules govern the naming of compounds. The student should practice the exercises at the end of this chapter until he has mastered the writing and naming of formulas.

ELEMENTS.... monatomic: most solids; the inert gases. Examples: Fe, Na, S, He, Ne, A.
    diatomic: most gases. Examples: $Cl_2$, $O_2$, $N_2$, gaseous $I_2$, $H_2$.

IDE.... Compounds ending in *ide* are made up of two elements only. This class includes
    Metal plus non-metal. Example: CaO, calcium oxide; $AlCl_3$, aluminum chloride.
    Non-metal plus non-metal. Example: CO, carbon monoxide; $NO_2$, nitrogen dioxide.
    Exceptions to rule are the compounds containing the hydroxyl radical (OH) and $NH_4^+$. These end in *ide* even though they contain three elements. Examples: NaOH, sodium hydroxide; $Ca(OH)_2$, calcium hydroxide; $NH_4Cl$, ammonium chloride.

OUS and IC. Compounds which contain metals which may have several valences are distinguished by ending the name of the metal with *ous* or *ic*. *Ous* is used to designate the lower valence of the metal; *ic* is for the higher valence. Example: $Cu^{+1}Cl^{-1}$, cuprous chloride; $Cu^{+2}Cl_2^{-1}$, cupric chloride; $Hg_2^{+1}O^{-2}$, mercurous oxide; $Hg^{+2}O^{-2}$, mercuric oxide.

MONO, DI, etc. Compounds formed by the combination of two non-metals which may have variable valence are distinguished by the prefixes *mono, di, tri, tetra, penta.* Examples: CO, carbon monoxide; $CO_2$, carbon dioxide; $P_2O_3$, phosphorus trioxide; $N_2O_5$, nitrogen pentoxide.

ITE and ATE. The *ite* compounds have not been mentioned before. When a compound consists of a metal plus a non-metal plus oxygen, the non-metal may have several valences. Thus we have $KCl^{+3}O_2$ and $KCl^{+5}O_3$. To distinguish between the two, the compound containing chlorine with the lower valence is called potassium chlorite ($KClO_2$), while the one with the higher valence is potassium chlorate ($KClO_3$).

As a further illustration, let us take the common acids and the potassium derivatives formed from the compound radicals tabulated in section 56.

Non-metal of lower valence

| | |
|---|---|
| Chlorous acid $HClO_2$ | $KClO_2$ potassium chlorite |
| Nitrous acid $HNO_2$ | $KNO_2$ potassium nitrite |
| Sulfurous acid $H_2SO_3$ | $K_2SO_3$ potassium sulfite |

Non-metal of higher valence

| | |
|---|---|
| Chloric acid $HClO_3$ | $KClO_3$ potassium chlorate |
| Nitric acid $HNO_3$ | $KNO_3$ potassium nitrate |
| Sulfuric acid $H_2SO_4$ | $K_2SO_4$ potassium sulfate |
| Carbonic acid $H_2CO_3$ | $K_2CO_3$ potassium carbonate. |

The last three are our most common acids, and their formulas should be memorized.

Note that the *ous-ic* terminology which was applied to lower-higher valences of metals in binary compounds is also applied to lower-higher valences of non-metals in these ternary compounds. In fact the *ous-ic* nomenclature is occasionally applied to lower-higher valences in binary compounds containing two non-metals, for example $SO_2$ sulfur*ous* oxide, $SO_3$ sulfur*ic* oxide; $PCl_3$ phosphor*ous* chloride, $PCl_5$ phosphor*ic* chloride, although the names sulfur dioxide, sulfur trioxide, etc., are in more general use.

**58. Review in the Writing of Equations.**—The student will be held responsible for all of the equations studied to date. He should also master the balancing of equations as given at the end of this chapter.

**59. Valence Changes During Oxidation and Reduction.**—Let us consider the changes in valence which have occurred during the following reactions:

(a) $2Hg^0 + O_2^0 \rightarrow 2Hg^{+2}O^{-2}$

(b) $Fe^0 + H_2^{+1}O^{-2} \rightarrow Fe^{+2}O^{-2} + H_2^0$

(c) $Cu^{+2}O^{-2} + H_2^0 \rightarrow Cu^0 + H_2^{+1}O^{-2}$.

In these reactions the substances oxidized are $Hg^0$ oxidized to $Hg^{+2}$; $Fe^0$ oxidized to $Fe^{+2}$; $H_2^0$ oxidized to $H_2^{+1}$. The substances reduced are $O_2^0$ reduced to $2O^{-2}$; $H_2^+$ reduced to $H_2^0$; $Cu^{+2}$ reduced to $Cu^0$. In each of these cases the substance oxidized has increased in valence, the substance reduced has reduced in valence (considering, for example, a change from 0 to −2 as a decrease).

Now these valence changes correspond to certain changes in the number of planetary electrons around each atom. For example, the mercury in the first equation became a mercuric ion by losing two electrons; while the copper ion in the last equation gained two electrons and became a copper atom:

$$Hg^0 - 2e \rightarrow Hg^{+2},$$
$$Cu^{+2} + 2e \rightarrow Cu^0.$$

When the mercury was oxidized, it gained in valence and lost electrons; when the copper ion was reduced it reduced in valence and gained electrons. Generalizing we may state **that reduction is a reduction in valence corresponding to a gain of electrons; while oxidation is an increase in valence corresponding to a loss of electrons.** Similarly, when magnesium is burned in air there is an oxidation-reduction reaction involving a transfer of electrons:

$$\begin{array}{l} 2Mg^0 + O_2^0 \rightarrow 2Mg^{+2}O^{-2}. \\ \ \ \downarrow \qquad \uparrow \\ 2 \times 2e = 4e \end{array}$$

This leads to a broad concept of oxidation-reduction, in which any changes in valence are called oxidation or reduction. For example, in the follow reaction iron is oxidized and sulfur is reduced:

$$\begin{array}{l} Fe^0 + S^0 \rightarrow Fe^{+2}S^{-2}. \\ \quad \searrow \ \nearrow \\ \qquad 2e \end{array}$$

## QUESTION REVIEW

**Symbols and Valence (54)**
**Valence of Some Compound Radicals (56)**
**Review and Extension of Nomenclature (57)**

Questions 1–50 which follow constitute a 30-minute quiz to be given in class. The student should prepare for this quiz by memorizing symbols, valences and nomenclature.

SECTION A. 15 seconds each (time 4 min.)

*Give symbols and valences for:* (1) magnesium, (2) potassium, (3) a metal with a valence of +3, (4) a non-metal with a constant valence of −2, (5) cuprous ion, (6) mercurous ion, (7) ferrous ion, (8) mercuric ion, (9) sulfur, (10) phosphorus, (11) chlorine, (12) zinc, (13) iodine, (14) hydrogen, (15) sodium.

SECTION B. 30 seconds each (time 7½ min.)

*Give formulas for the following:* (16) sodium chloride, (17) magnesium chloride, (18) zinc iodide, (19) aluminum chloride, (20) aluminum oxide, (21) carbon dioxide, (22) sulfur trioxide, (23) phosphorus pentoxide, (24) ferrous oxide, (25) mercurous chloride, (26) mercuric sulfide, (27) ferrous sulfide, (28) carbon monoxide, (29) cuprous chloride, (30) ferric iodide.

SECTION C. 45 seconds each (time 7½ min.)

*Give formulas for the following:* (31) potassium carbonate, (32) potassium sulfite, (33) zinc sulfite, (34) calcium nitrate, (35) silver nitrate, (36) calcium carbonate, (37) sodium carbonate, (38) aluminum carbonate, (39) potassium sulfate, (40) hydrogen chloride.

SECTION D. 1 minute each (time 10 min.)

*Give formulas for the following:* (41) cuprous nitrate, (42) ferrous chlorate, (43) mercuric sulfate, (44) ferric sulfate, (45) mercurous sulfide, (46) ferric chloride, (47) mercurous chlorite, (48) mercuric nitrate, (49) ferric nitrate, (50) cuprous sulfide.

51. Name the following substances. Try to recall the connection in which each has been mentioned thus far in the text. $FeS$, $H_2O$, $KClO_3$, $MgO$, $CuSO_4$, $AgNO_3$, $NaCl$, $AgCl$, $NaNO_3$, $HgO$, $BaO$, $BaO_2$, $H_2O_2$, $SO_2$, $H_2SO_3$, $CO_2$, $H_2CO_3$, $P_2O_5$, $Mg(OH)_2$, $NaOH$, $KOH$, $Ca(OH)_2$, $Fe_3O_4$, $FeO$, $ZnSO_4$, $CO$, $NH_3$, $CuO$, $H$, $MgCl_2$, $AlCl_3$, $CH_4$, $HCl$.

52. Write the formulas for the oxides, sulfides, carbonates, and nitrates of sodium, copper ($Cu^{II}$), and aluminum.

53. Correct the following formulas: $CaNO_3$, $PbCl$, $AgCl_2$, $Mg_2CO_3$, $(NH_4)_2Cl$, $Ca(OH)$, $ZnS_2$, and $P^VO_5^{II}$.

54. Name the substances having the following formulas: $FeCO_3$, $Fe_2(SO_4)_3$, $CaBr_2$, and $Mg(NO_3)_2$.

55. Mark the valences of the simple and compound radicals in the following substances: $KNO_3$, $CaSO_4$, $ZnCO_3$, $Fe(NO_3)_2$, $Fe(NO_3)_3$, $Al(OH)_3$, $Al_2S_3$. Write the names of these substances.

### Experimental Evidence for Valence: electrical, chemical, atomic structure (55)

56. What three lines of independent evidence indicate that aluminum has a valence of $+3$, while sodium has a valence of $+1$?

57. Define and illustrate: electron, ion, atom, planetary electron, electrolysis, electroplating, displacement, inert gas, compound radical.

58. 20 grams of a given element liberates 11.2 liters of hydrogen from acids. What element is it? To answer this make use of the table of elements on the inside back cover of the text.

59. If 18 g. of aluminum displaces 2 g. of hydrogen from hydrochloric acid, what is the valence of the metal?

60. How may the valence of a non-metal be determined by chemical means?

61. Give one valence each for atoms with atomic numbers 12, 13, 14 and 15 respectively.

62. Nitrogen has an atomic number of 7. Calculate two valences it may have on the basis of atomic structure.

63. Show why, on the basis of atomic structure carbon, atomic number 6, may have valences of $+4$ and $-4$.

### Review in the Writing of Equations (58)

### •SECTION E. BALANCE THE FOLLOWING EQUATIONS

64. Hydrogen plus chlorine gives hydrogen chloride.
65. Sulfur heated in oxygen gives sulfur dioxide.
66. Phosphorus plus oxygen gives phosphorus pentoxide.
67. Sulfur dioxide plus oxygen gives sulfur trioxide.
68. Hydrogen atom plus hydrogen atom gives hydrogen molecule.
69. Chlorine plus iodide ion gives iodine plus chloride ion.
70. Zinc plus phosphorus gives zinc phosphide.
71. Iron plus oxygen gives ferric oxide.
72. Sodium nitrate heated gives sodium nitrite plus oxygen.
73. Calcium carbonate plus hydrogen sulfate gives calcium sulfate plus hydrogen carbonate; the latter then breaks down into water and carbon dioxide.

### SECTION F. COMPLETE AND BALANCE THE FOLLOWING EQUATIONS

74. Mercuric oxide heated.
75. Hydrogen plus oxygen.

76. Iron heated with sulfur.
77. Sodium plus chlorine.
78. Copper sulfate plus iron.
79. Silver nitrate plus sodium chloride.
80. Potassium sulfate plus barium chloride.
81. Calcium oxide plus hydrogen chloride.
82. Potassium iodide plus chlorine.
83. Calcium carbonate plus hydrogen chloride (see question 73).

84. Write equations to show the following: (1) formation of $FeSO_4$ from iron and sulfuric acid, (2) formation of $ZnCl_2$ from zinc and hydrochloric acid, (3) the reduction of cupric oxide by hydrogen, (4) the action of steam upon hot zinc, and (5) the action of hydrochloric acid upon zinc carbonate.

### Valence Changes During Oxidation and Reduction (59)

85. In the following reactions, state whether oxidation and reduction have occurred. Tell what is oxidized and the valence changes it has undergone.

*a.* $Mg + 2HCl \rightarrow MgCl_2 + H_2 \uparrow$
*b.* $Cl_2 + 2NaI \rightarrow 2NaCl + I_2$
*c.* $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$
*d.* $2KClO_3 \rightarrow 2KCl + 3O_2 \uparrow$

86. Define oxidation and reduction in terms of changes in valence, and loss or gain of electrons. Illustrate.

# CHAPTER VII

# WATER

**60. History of Water** —To the ancients water was one of the four elements (5); and this idea persisted down through the middle ages. It was hence a revolutionary discovery when in 1781 Cavendish announced that water was obtained from burning hydrogen. But he was so imbued with the phlogistic explanation of combustion (30) that he did not fully appreciate the discovery; and it remained for Lavoisier to repeat Cavendish's experiments two years later at which time he showed that water was not a simple substance but a compound.

**61. The Composition of Water.**—Following this discovery, water was the object of many researches, since its relatively simple composition lent itself to quantitative investigations. In particular the relative amounts of hydrogen and oxygen in the compound were carefully determined. These researches have followed two lines: determining the relative (*a*) weights and (*b*) volumes of the two elements in the compound. We shall now follow these in detail.

## a. Composition of Water by Weight.

Berzelius and Dulong (1819) and Dumas and Stas (1842) determined the composition of water by indirect weighing (Fig. 27), as illustrated in the following equation:

$$\underset{\substack{\text{weigh}\\ W_1}}{\mathrm{CuO}} + \mathrm{H_2} \rightarrow \underset{\substack{\text{weigh}\\ W_2}}{\mathrm{Cu}} + \underset{\substack{\text{(weigh after}\\ \text{absorbing}\\ \text{in CaCl}_2\text{)}\\ W_3}}{\mathrm{H_2O}},$$

where

$$\frac{\text{wt. } O}{\text{wt. } H} = \frac{W_1 - W_2}{W_3 - (W_1 - W_2)}.$$

As a result of nineteen experiments, Dumas and Stas found that 840.161 g. of oxygen yielded 945.439 g. of water. This gives an oxygen : hydrogen ratio of 840.161 : 105.278 which, translated into our modern standards where oxygen is 16, gives the ratio 16 : 2.0050.

This value was accepted until 1888 when Cooke and Richards carried out experiments leading to the ratio 16.000 : 2.0126.

Edward Morley, an American chemist at Western Reserve University, was the first to make an accurate determination by the direct weighing of the oxygen gas, hydrogen gas, and water. The hydrogen was absorbed in palladium (49) and weighed, while the oxygen was weighed in a large globe. The water formed from their combination was frozen out and weighed. Morley reported a ratio of 16.000 : 2.016 at the first general meeting of the American Chemical Society in 1893.

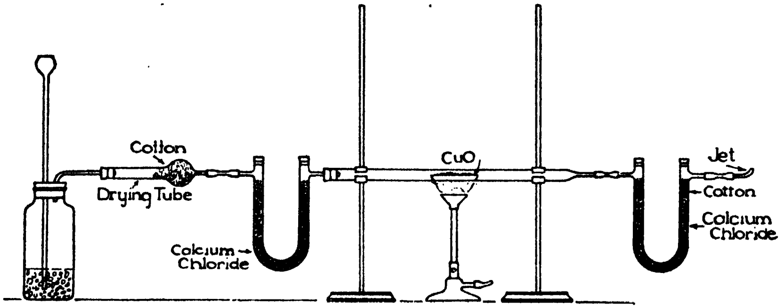


FIG. 27. Dumas method for determining composition of water by weight. Hydrogen passed over hot copper oxide forms water, which is absorbed in a weighted U-tube containing calcium chloride.

It is interesting to compare the values of the above researches with the results of the most recent work of the twentieth century. The International Committee on Atomic Weights sanctioned an atomic weight of 1.0080 for hydrogen in 1941, which corresponds to the ratio 16.000 : 2.0160.

**b. Composition of Water by Volume.**

When 2 volumes of hydrogen mixed with 1 volume of oxygen ("electrolytic gas") are exploded in a simple eudiometer by means of an electric spark, the steam condenses and the gases vanish. In case different proportions are mixed and exploded, either hydrogen or oxygen will be left over.

The **eudiometer** (Greek, meaning *fine weather* + *-meter*) is an instrument for measuring gases by volume; so named because it is frequently used to determine the purity of the air. It was employed by Cavendish.

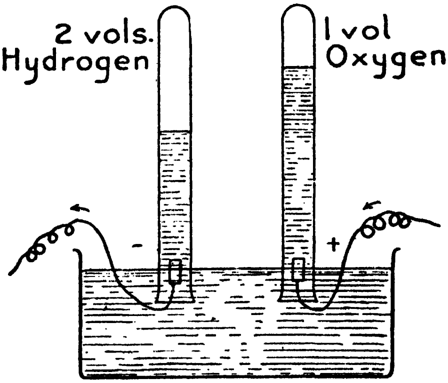


FIG. 28. Electrolysis of water.

### DEMONSTRATION 24. VOLUMES OF HYDROGEN AND OXYGEN COMBINING TO FORM WATER

Materials: Apparatus shown in Fig. 29 and described below.

If the experiment just described is performed in a eudiometer surrounded by a steam jacket, the water is obtained as steam, and its volume thus found (Fig. 29). Hydrogen and oxygen (electrolytic gas) are generated by the electrolysis of water containing in solution a small quantity of sodium hydroxide. The carefully dried gases, say, 20 cc. of hydrogen and 10 cc. of oxygen, are passed into the eudiometer, and are confined above mercury. An electric spark produced by an induction coil is passed through the mixture, which causes an explosion, with the production of water vapor. The volume of gas decreases. The temperature remains constant throughout (100°), and the tube containing the steam is so adjusted that its volume is read off under the same pressure as that of the combining gases. Approximately 20 cc. of steam should be obtained. The volume of steam is, therefore, equal to the volume of the hydrogen and to double that of the oxygen:

$$\underset{\substack{\text{Hydrogen} \\ \text{2 volumes}}}{2H_2} + \underset{\substack{\text{Oxygen} \\ \text{1 volume}}}{O_2} \rightleftarrows \underset{\substack{\text{Steam} \\ \text{2 volumes}}}{2H_2O}.$$

**62. Gay-Lussac's Law of Combining Volumes of Gases.**—It may at first perplex the reader to learn that three volumes of gas ($2H_2 + 1O_2$) shrink to two volumes of steam. A picture of what has occurred, in terms of molecules, will perhaps help (Fig. 30). These atoms have been drawn to scale. Notice that hydrogen occupies as large a square as oxygen. This concept was formulated in 1811 by an Italian scientist, Avogadro, when he postulated **that at any given pressure and temperature equal volumes of different gases contain the same number of molecules.** Thus, although the size of the hydrogen molecule is considerably less than that of the oxygen molecule, both molecules occupy the same amount of space. A plausible explanation is that the molecules are all in constant motion, and the smaller the molecule the faster it moves; and that these two effects, size and mobility, cancel one another.

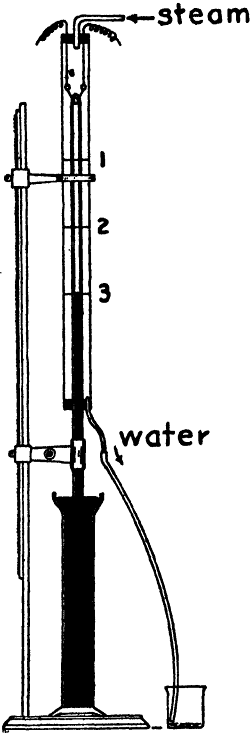


FIG. 29. Composition of water by volume. (Demonstration 24.) A mixture of hydrogen and oxygen is exploded in a tube surrounded by steam.

It may also surprise the reader to see that exactly whole numbers are involved; that is, that 2 volumes of hydrogen require exactly 1 volume of oxygen, and that exactly 2 volumes of steam are formed. Such a relationship is not unique for water. Thus in the formation of ammonia:

$$N_2 + 3H_2 \rightarrow 2NH_3,$$

one volume of nitrogen combines with

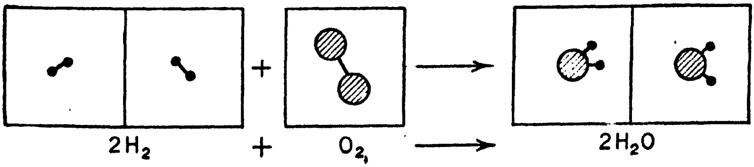


FIG. 30. Combination of *electrolytic gas.*

three volumes of hydrogen, to form two volumes of ammonia. In the reaction

$$H_2 + Cl_2 \rightarrow 2HCl,$$

the ratio of the reacting volumes is 1 : 1 : 2.

These data illustrate a recurrent phenomenon in nature which Gay-Lussac formulated into a law in 1808. It states that **when gases combine chemically, they do so in volumes which bear a simple ratio to one another, and to the volume of the product, if gaseous.**

It is understood, of course, that the volumes of all the gases are measured under the same conditions of pressure and temperature.

The reason for this remarkable regularity in nature becomes apparent when one accepts the concept of molecules and the postulate of Avogadro stated above. For in that case the words "molecule" and "volume" are interchangeable, as in

$$\begin{array}{ccccc} 2H_2 & + & O_2 & \rightarrow & 2H_2O. \\ \text{2 molecules} & + & \text{1 molecule} & \rightarrow & \text{2 molecules} \\ \text{2 volumes} & + & \text{1 volume} & \rightarrow & \text{2 volumes} \end{array}$$

**63. Occurrence of Water.**—Water covers about three-fourths of the earth's surface, the greatest depth of the ocean being about 6 miles. Water vapor rises continuously from the surface of the sea and is condensed in colder regions, appearing as clouds and fog, or is precipitated as rain, snow, or sleet. Water vapor is an important component of the air. Even the "dry" land contains considerable quantities of water. Water also constitutes a large part of organisms and of many common materials. For example, about 70% of the human body, 74% of eggs, 87% of milk, 92% of watermelons, 94% of tomatoes, and 95% of cucumbers is water. The presence of water in organic matter may be shown by heating pieces of an apple or of a potato in a clean test-tube.

**64. Natural Waters.**—No water found in nature is perfectly pure. Rain is virtually distilled water; but when it falls, various gases and solids, such as nitrogen, oxygen, carbon dioxide, and ammonium nitrate, are dissolved; also, insoluble matter, such as particles of dust, pollen grains, and bacteria is carried down. Moreover, when water percolates through the soil, it has a solvent action upon various substances, such as limestone and calcium sulfate. The water finding its way into rivers, lakes, and oceans contains not only matter in solution, but suspended matter.

Even clear spring water and rain water are not pure. The impurities found in water can be divided into two classes:

(*a*) *Mechanically suspended impurities;*
(*b*) *Soluble impurities.*

## a. Mechanically Suspended Impurities.

### DEMONSTRATION 25. PURIFICATION OF WATER

Materials: Cylinder of clear water, cylinder of muddy water, aluminum sulfate, ammonium hydroxide, filter paper, large test-tube, funnel, funnel containing pebbles and sand, water-cooled still in operation, potassium permanganate.

Suspended impurities may be removed from water (1) by filtration, or (2) by allowing the suspended matter to settle.

On a large scale, the process of filtration is carried out by means of beds of sand and gravel. Most of the suspended matter, including bacteria, is removed (Fig. 31).

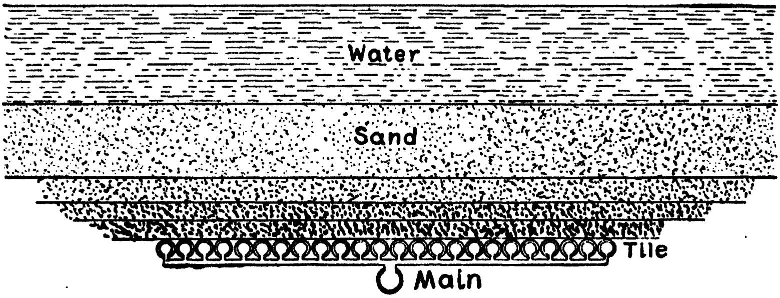


FIG. 31. Filtration of water.

Water is also run into large settling tanks, and small amounts of alum, aluminum sulfate, or other substances are added; a slimy precipitate is formed, and suspended matter, including microorganisms, attaches itself to the gelatinous precipitate and is finally carried to the bottom of the tank. With water containing the requisite amount of alkalinity, a flocculent precipitate of aluminum hydroxide is formed.

Even after filtration or the coagulation treatment, water still contains some bacteria. To make it safe for drinking, small quantities of germicides are added, such as chlorine or bleaching powder. Water is also treated with ozone and with ultra-violet light. Water may also be purified by distillation. The Liebig still is quite generally employed in laboratories for distilling liquids (Fig. 32).

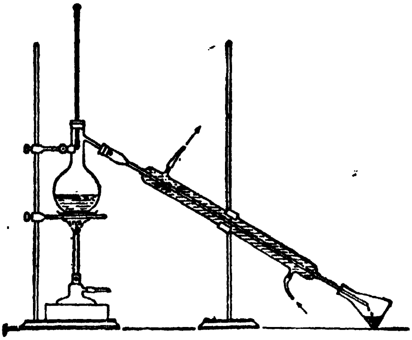


FIG. 32. Distillation apparatus.

**b. Soluble Impurities.**

Waters containing soluble impurities may be divided into a number of classes, some of which are:

(1) **Soft waters,** which are comparatively free from mineral salts. They are found in districts where quartz sand and sandstone occur.

(2) **Hard waters,** which contain in solution certain mineral salts, especially the salts of calcium and of magnesium. They are found in limestone and dolomite districts; also where gypsum occurs. Hard waters are objectionable, for they consume large quantities of soap and often form boiler-scale, which means that a larger amount of fuel is required to generate steam. It has been estimated that a layer of scale a quarter of an inch thick on the boiler tubes requires 50 per cent more fuel in generating steam. It is difficult to remove boiler-scale; and now and then the thick scale cracks, thus exposing very hot iron to steam, causing an explosion (46, 2).

(3) **Mineral waters** contain other impurities: carbon dioxide (effervescent waters); alkali metal salts (Vichy); iron salts (Chalybeate); sulfur compounds (White Sulfur Springs); and sulfates (Bitter or Saline waters).

**65. Formation.**—Water is formed (a) during the burning of hydrogen or organic compounds; (b) during the reduction of oxides with hydrogen; and (c) by the interaction of a metallic hydroxide and an acid (neutralization):

a. $$\begin{cases} 2H_2 + O_2 \rightarrow 2H_2O \\ CH_4 + 2O_2 \rightarrow 2H_2O + CO_2 \end{cases}$$

b. $$CuO + H_2 \rightarrow Cu + H_2O$$

c. $$KOH + HNO_3 \rightarrow KNO_3 + H_2O.$$

### 66. Physical Properties of Water.—

TABLE 13. PHYSICAL PROPERTIES OF WATER

| | | | |
|---|---|---|---|
| $d_{H_2O\ liq.}$ 25° C. | | | 0.997 |
| $d_{H_2O\ liq.}$ 3.98° C. | | | 1.0000 |
| $d_{H_2O\ liq.}$ 0° C. | | | 0.999 |
| $d_{H_2O\ ice}$ 0° C. | | | 0.917 |
| B.P. | 100° C. | 212° F. | 373° A. |
| M.P. | 0° C. | 32° F. | 273° A. |
| Heat of vaporization | | | 540 cals. |
| Heat of fusion of ice | | | 79 cals. |

Pure water is a clear, tasteless, odorless liquid; it is colorless when viewed in moderate quantity, but when seen in bulk, it possesses a bluish-green color. Some lake waters which are relatively pure, however, have a brownish hue on account of organic matter. Thus, the water of Loch Katrine, in Scotland, is nearly chemically pure, but it has a perceptible brownish tint due to traces of organic matter taken up from the peat of the surrounding country.

DEMONSTRATION 26. WATER AS A POOR CONDUCTOR

Materials: Test-tube of water, piece of lead, lump of ice, test-tube holder, burner.

Water is a poor conductor of heat, as may be shown by placing a piece of lead above a lump of ice contained in a test-tube three-fourths full of water, and then heating the water to boiling in the upper part of the tube.

When water is heated or cooled at temperatures above 4° C. it follows the general law that bodies expand when heated, and contract when cooled. When cooled from 4° to 0° C., however, it expands; and upon being heated from 0° to 4° it contracts, reaching its maximum density at 4° C. (really 3.98° C.). This is shown in table 14.

TABLE 14. DENSITY OF WATER IN GRAMS PER CUBIC CENTIMETER

| t° C. | Density | t° C. | Density |
|---|---|---|---|
| 0 | 0.999867 | 6 | 0.999968 |
| 1 | 0.999926 | 10 | 0.999727 |
| 2 | 0.999968 | 15 | 0.999126 |
| 3 | 0.999992 | 20 | 0.998229 |
| 3.98 | 1.000000 | 25 | 0.997069 |
| 5 | 0.999992 | 30 | 0.995672 |

Notice the abnormal behavior of water between 0° C. and 4° C. Ice is less dense than water at 0° C. As a result, ice forms on the surface of ponds. If this were not so, our large bodies of fresh water would be converted into solid masses of ice during long, cold winters, which the warmth of summer would not be sufficient to melt. 11 volumes of ice melt into 10 volumes of water at 0° C.

**The weight of 1 cc. of water at 4° C. is 1 gram, which is the unit of density.** Other properties for which water is used as a standard include the **Centigrade temperature scale** (79), the **calorie** (39), and **specific heat.** The high specific heat of water (compare $H_2O$ 1, Fe 0.1, Pb 0.03) means that more heat is required to warm water than most substances, so that the temperature changes of large masses of water are more gradual than are those of the land. This means that a continental climate is not as even as that of an island.

It requires 79 calories to convert 1 g. of ice at 0° into liquid. The **heat of fusion of ice** is therefore said to be 79 thermal units. A mixture of water and ice, at equilibrium, has a temperature of 0°—the melting point, or the freezing point, of water. If the mixture is heated, the temperature strangely enough will not rise so long as any ice is present. Instead, the heat is consumed as heat of fusion, and more ice melts. After the last particle of ice has melted, additional heat will cause the temperature of the liquid to rise.

**67. Pressure of Aqueous Vapor.**—When water is left in an open dish, evaporation takes place and the water eventually disappears into the air. This is because molecules of liquid are constantly in motion; and some of the molecules leave the surface of the water and do not return. They have become gaseous, aqueous vapor. If this same water is confined, however, such as in a half-filled, stoppered bottle the water will not disappear.

This is because the gas space above the surface of the water in the bottle eventually becomes so filled with aqueous vapor composed of water molecules in constant motion that there are as many water molecules returning to the surface of the liquid as there are molecules escaping into the gas (Fig. 33). We say that a state of equilibrium has been reached, resulting in a certain gaseous pressure of the aqueous vapor. This pressure will be greater the higher the temperature of the liquid. Careful measurements have shown that at equilibrium the following aqueous pressures would be reached in the bottle:

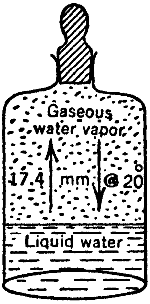


FIG. 33. State of equilibrium in a closed system.

TABLE 15. VAPOR PRESSURES OF WATER EXPRESSED IN MILLIMETERS OF MERCURY

| | | | |
|---|---|---|---|
| 0° | 4.6 | 26° | 25.0 |
| 5° | 6.5 | 27° | 26.5 |
| 10° | 9.1 | 28° | 28.1 |
| 11° | 9.8 | 29° | 29.7 |
| 12° | 10.4 | 30° | 31.5 |
| 13° | 11.1 | 40° | 54.9 |
| 14° | 11.9 | 50° | 92.0 |
| 15° | 12.7 | 60° | 148.9 |
| 16° | 13.5 | 70° | 233.3 |
| 17° | 14.4 | 80° | 354.9 |
| 18° | 15.3 | 90° | 525.5 |
| 19° | 16.3 | 97° | 681.9 |
| 20° | 17.4 | 100° | 760.0 |
| | | | (1 atmos.) |
| 21° | 18.5 | 120° | 1491.3 |
| 22° | 19.6 | 150° | 3581.2 |
| 23° | 20.9 | 180° | 7546.4 |
| 24° | 22.2 | 220° | 17390.4 |
| 25° | 23.7 | | (25 atmos.) |

You will notice from the table that at 100° C. the aqueous pressure is 760 mm. In other words, when water is heated up to 100° C. the pressure of molecules escaping from its surface becomes equal to the normal pressure of the atmosphere (760 mm). That is why the water boils and escapes. A liquid boils when its vapor pressure becomes equal to the pressure of the atmosphere. On the summits of mountains, where the pressures are lower, water and other liquids have lower boiling points. At Quito, for example, which is 2,914 meters above the level of the sea, the mean height of the barometric column is 523 mm.; therefore the boiling point of water is only 89.9°. You would not relish a "three-minute egg" at Quito. Even snow and ice have an aqueous pressure; for this reason clothes hung out on an icy day continue to lose water even though they are frozen stiff.

### DEMONSTRATION 27. AQUEOUS TENSION AND TEMPERATURE

Materials: Mercury barometer, jacketed near the top with a tube; hot water, ink dropper with curved tip.

Aqueous pressure may be visualized by introducing a drop of water at the bottom of a mercury barometer. The water immediately rises to the top of the mercury and depresses the latter considerably (Fig. 34). Hot water is then poured into the jacket. This increases aqueous pressure and depresses the mercury still further. The hotter the water the greater the depression.

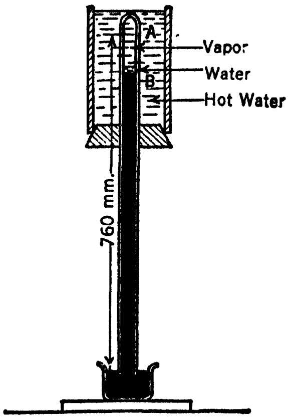


FIG. 34. Depression of mercury column by aqueous tension.

The vapor pressure of a liquid at equilibrium is called its vapor tension; for water this is called **aqueous tension.** A space is said to be saturated with water vapor when water at a certain temperature has the given maximum amount of vapor permitted by its aqueous tension. The air, in general, is less than two-thirds saturated. When it is greater than that it is uncomfortable for living, and we complain about the humidity.

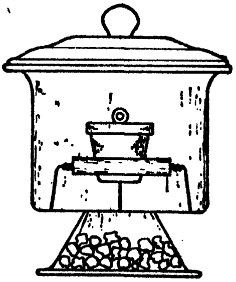


FIG. 35. A desiccator.

Whenever gases are collected over water, aqueous vapor is always mixed with the gases. All bodies and substances when exposed to the atmosphere have more or less water condensed upon their surfaces. In order to get rid of traces of water, the body or substance is heated, and then allowed to cool in a **desiccator** (Fig. 35). A desiccator is a glass vessel with an air-tight cover; it contains some desiccating agent, such as calcium chloride or concentrated sulfuric acid.

**68. Deliquescence.**—The vapor tension of concentrated water solutions of substances is often less than the aqueous pressure in the air. Consequently water will pass readily from the air into these solutions. When certain very soluble substances, such as the chlorides of magnesium, calcium, and zinc, are exposed to the air, they first become moist, and finally go into solution. This is due to the fact that when the solid comes in contact with the moisture in the air, water is absorbed and a very concentrated solution is formed on the surface of the crystal. As the vapor tension of this solution is less than the partial pressure of the water vapor in the air, more moisture is taken up from the air until the solid goes entirely into solution. As more water is absorbed, the solution becomes more dilute, and this will continue until the vapor pressure of the solution becomes equal to the aqueous pressure of the air above it. This deportment is known as **deliquescence.**

### DEMONSTRATION 28. DELIQUESCENCE

Materials: Two 400-cc. beakers, bell jar on plate of glass, vaseline, magnesium chloride.

One beaker is half filled with distilled water; the other with an equal volume of a concentrated solution of magnesium chloride. The beakers are placed in an air-tight bell jar and left at room temperature for a year (Fig. 36). Water gradually evaporates from one vessel and is absorbed in the other. Common table salt contains a small amount of magnesium chloride which deliquesces, particularly at the seashore or in humid weather.

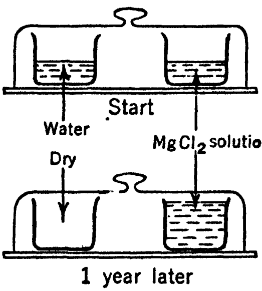


FIG. 36. Deliquescence of magnesium chloride.

**69. The State of Equilibrium.**—When a drop of water is introduced into a mercury barometer, as in Section 67, there are at first no molecules of water vapor above the liquid. The number of molecules of water passing into the state of vapor is constant per unit of time, being determined by the aqueous tension of water at the given temperature. The number plunging back into the liquid is zero at first, but gradually increases until the number returning to the liquid state is just equal to the number leaving. When this condition is reached, it is called *kinetic equilibrium*, for it is dynamic and not static.

**70. Chemical Properties of Water.**—*a.* Water is a stable compound. At high temperatures, however, it **dissociates** into its elements:

$$2H_2O \rightleftarrows 2H_2 + O_2.$$

At 2,650° and 1 atmosphere of pressure, water is 11 per cent dissociated; at 2,000°, 1.8 per cent (less than 2 molecules of steam in every hundred are dissociated). The dissociation increases with increased temperature and decreased pressure. The breaking down of water into its constituents is called **dissociation**; the reuniting of hydrogen and oxygen to form water is called **association.** Note that the breaking down of potassium chlorate ($KClO_3$), when heated, is called decomposition, for the action is not reversible.

*b.* Water interacts with the more active metals to form hydrogen (46).

*c.* Water interacts with oxides of non-metals to form acids; and with oxides of metals to form metallic hydroxides (35).

*d.* Water combines with a number of substances to form hydrates (71).

**71. Hydrates and Efflorescence.**—Many substances on crystallizing from aqueous solutions unite with water to form compounds known as hydrates. Some common hydrates follow.

| | |
|---|---|
| Blue vitriol (copper sulfate) | $CuSO_4, 5H_2O$ |
| Barium chloride | $BaCl_2, 2H_2O$ |
| Epsom salt (magnesium sulfate) | $MgSO_4, 7H_2O$ |
| Washing soda (sodium carbonate) | $Na_2CO_3, 10H_2O$ |
| Glauber's salt (sodium sulfate) | $Na_2SO_4, 10H_2O$ |

Many salts crystallize from water without combining with it, such as:

| | |
|---|---|
| Sodium chloride | $NaCl$ |
| Potassium chlorate | $KClO_3$ |
| Potassium dichromate | $K_2Cr_2O_7$ |

### DEMONSTRATION 29. HYDRATES

**Materials:** Test-tube, anhydrous copper sulfate, hydrated copper sulfate, test-tube holder, filter paper, wash bottle, burner.

When a hydrate is heated, it gives up water. This may be shown by heating a crystal of the hydrate, blue vitriol, in a clean, dry test-tube. Water deposits upon the colder part of the tube, and a powder—the anhydrous salt—is left in the test-tube. Anhydrous copper sulfate is whitish. If a little of the powder be sprinkled on a piece of filter paper and then moistened with water, it turns blue and heat is liberated, on account of the formation of the hydrated salt:

$$\underset{\text{(White)}}{\text{Copper sulfate}} + \text{Water} \rightleftarrows \underset{\text{(Blue)}}{\text{Hydrated copper sulfate}} + \text{Heat.}$$

The action is reversible.

Are hydrates definite chemical compounds? If so, their composition should conform to the law of constant proportions and there should be a definite chemical formula for every hydrate. Chemical analysis shows that hydrates have definite or constant composition; they are, therefore, chemical compounds. Solutions prepared by dissolving the hydrate and the anhydrous salt are identical, provided they are of equal concentration and density.

### DEMONSTRATION 30. EFFLORESCENCE

Materials: Clock-glasses containing the following substances exposed to the air overnight: blue vitriol, washing soda, Glauber's salt, sodium hydroxide, table salt, potassium dichromate.

Some hydrates, such as blue vitriol or gypsum, are very stable in the air; others, such as washing soda and Glauber's salt, lose water and crumble to powder. Every hydrate has a definite vapor pressure. $CuSO_4$ for example forms three hydrates, $CuSO_4, H_2O$ and $CuSO_4, 3H_2O$ and $CuSO_4, 5H_2O$: each has its own pressure. This is shown in Fig. 37. **Hydrates which, when exposed to the air in open vessels, have a vapor pressure greater than the partial pressure of the water vapor in the air, effloresce.** Thus, washing soda loses water when exposed to the air. Gypsum and blue vitriol, on the other hand, have vapor pressures less

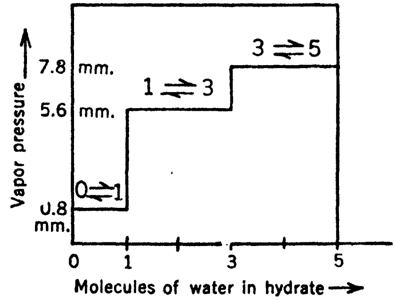


FIG. 37. Vapor pressures of the hydrates of copper sulfate at 25°.

than that of the partial pressure of the water vapor in the air; consequently they do not give up their water of hydration. Thus, the vapor pressure of blue vitriol at 25° is only 7.8 mm.; while the partial pressure of the water vapor of the atmosphere, which is usually less than two-thirds saturated at the given temperature, would be about 15 mm.

By referring to section 68 the student should distinguish in his own mind the difference between deliquescence and efflorescence. Deliquescence is a *physical* property, related to the aqueous tension of concentrated water solutions of any substance; efflorescence is a *chemical* property, related to the chemical dissociation of hydrates. Only hydrates can effloresce; any substance may deliquesce whether it is a hydrate or not.

**72. Uses for Water.**—Water is the substance most generally used **as a solvent.** Some solids, such as sugar and salt, are readily soluble in water; others, such as sea-sand (silica) and silver chloride, are so very slightly soluble that they are called "insoluble" substances. Liquids such as acetic acid and alcohol, dissolve in water in all proportions; whereas other liquids, such as ether, are sparingly soluble. Such gases as ammonia and hydrogen chloride are extremely soluble in water, carbon dioxide is sparingly soluble, and oxygen and hydrogen only slightly soluble. There is no known substance which is entirely insoluble in water. Even finely divided glass, quartz, gold, and platinum dissolve in minute amounts.

**In industry** enormous quantities of water are consumed for washing out traces of undesirable acids, alkalies, dyes, detergents, etc. For example the Texas Gulf Sulfur Company's new Gulf plant is equipped with a seven hundred million gallon water reservoir for forcing sulfur out of the ground.

**Water and health** go hand in hand. A pure water supply is very essential for the health of a city or community. In recent years so much attention has been given to the subject that typhoid fever is almost negligible in large cities. Water which is apparently pure may contain pathogenic organisms—germs of typhoid, cholera, or anthrax. To insure pure water for drinking, it should be examined frequently by the biologist and the chemist. The object of a bacteriological examination is to detect the numbers and kinds of organisms present. The detection of disease-producing organisms is a matter of considerable difficulty. Such an examination of water is chiefly valuable as a test of the efficacy of the processes used in its purification.

Chemical analysis of a water is more rapid than is a bacteriological examination, and though it leaves much to be desired, it affords valuable indications. Thus, if a water contains much nitrogen either in the form of albumin or albuminous matter, or as decomposition and oxidation products—ammonia, nitrites, or nitrates—it shows pollution with animal matter, likely sewage. A high content of chlorine as sodium chloride usually indicates sewage pollution. Wherever animal matter or sewage is present, disease-producing bacteria may be present also.

**73. Heavy Water.**—It will be recalled that a heavier type of hydrogen atom, called deuterium, was discovered in 1931 (52). By burning this heavy hydrogen with oxygen, a so-called **heavy water** is produced. Its density is actually about 10 per cent greater than ordinary water. Some interesting data follow.

TABLE 16. PHYSICAL PROPERTIES OF $H_2O$ AND $D_2O$

| $H_2O$<br>water<br>Discoverer: Cavendish, 1781 | | $D_2O$<br>heavy water<br>Discoverers: Urey and Washburn, 150 years later, 1931 | |
|---|---|---|---|
| $d_{H_2O}$ at 25° C. | 0.997069 | $d_{D_2O}$ at 25° C. | 1.1066 |
| B.P. | 100° C. | B.P. | 101.42° C. |
| M.P. | 0° C. | M.P. | 3.82° C. |
| Maximum density | 1.000 | Maximum density | 1.11 |
| at | 3.98° C. | at | 11.6° C. |

Heavy water has been a valuable research tool for the biologist. How long does the water we drink remain in our bodies? Until the discovery of $D_2O$ no experiment could be devised to answer this question. The water in the urine might come either from water drunk only a few hours previously, or from water stored in the body for years. But take a drink of heavy water; and how long will it be before the normal ratio 6,900 H to 1 D in the urine increases? To answer these questions Hevesey in 1934 first demonstrated that heavy water may be drunk with apparent impunity. Later he carried out the experiment suggested above: the heavy water began to appear in the urine and perspiration several hours after drinking; at the end of 15 days only half of it had been accounted for, and it took a full month to recover all of the heavy water from the body. The heavy hydrogen thus acted as a tag for these molecules whose biological action was in doubt.

Further biological researches of this nature will be presented in a later section (245).

## QUESTION REVIEW

### I. HISTORY OF WATER

**a. General (60).**

1. Why did Cavendish, who discovered hydrogen, fail to recognize that water is a compound?

**b. The Composition of water (61).**

2. Mention some of the attempts to determine the composition of water by weight and by volume.
3. Describe the Dumas and Stas indirect method.

**c. Gay-Lussac's law of combining volumes of gases (62).**

4. State Gay-Lussac's law of combining volumes. Show how this is substantiated by several reactions.
5. State Avogadro's law. How does it make the law of combining volumes plausible?
6. Why is it incorrect to say for the reaction $Fe + S \rightarrow FeS$ that 1 volume of iron combines with 1 volume of sulfur to give 1 volume of ferrous sulfide?
7. What volume of gas at 0° is obtained when 150 cc. of hydrogen is exploded with 60 cc. of oxygen?

### II. OCCURRENCE OF WATER (63–64).

8. What are the approximate percentages of water in some common materials?
9. How are mechanically suspended impurities removed?
10. Mention some materials found in soft and in hard waters.

### III. FORMATION OF WATER (65).

11. State three methods for forming water.

### IV. PHYSICAL PROPERTIES OF WATER.

**a. General (66).**

12. State some physical properties of water such as color, compressibility, B.P., M.P., conductivity.
13. Why do not lakes freeze *en masse*?
14. Define and illustrate calorie, specific heat, heat of fusion, heat of vaporization, boiling point in terms of vapor pressure.

**b. Pressure of aqueous vapor (67).**

15. When is a given space said to be saturated with water vapor?
16. Why would a 3-minute egg boiled in water on the summit of a mountain two miles above sea level be unpalatable?

17. Describe the apparatus for demonstrating aqueous pressure.
18. Describe what occurs amongst the molecules when a bottle is half-filled with water, stoppered, and allowed to stand for a while at room temperature.
19. Sketch a desiccator.

**c. Deliquescence (68).**

20. Why does table salt become sticky at the sea shore?
21. Describe an experiment illustrating deliquescence.

**d. The state of equilibrium (69).**

22. Describe characteristics of the state of equilibrium.

V. CHEMICAL PROPERTIES OF WATER (70).

**a. General.**

23. Discuss association and dissociation. Differentiate between dissociation and decomposition.
24. State 3 different chemical reactions involving water.

**b. Hydrates and efflorescence (71).**

25. What is the difference between a hydrate and a hydroxide? Illustrate. What evidence have we that hydrates are definite chemical compounds?
26. Explain fully why some hydrates effloresce when exposed in open vessels, while others do not.
27. Distinguish between deliquescence and efflorescence. Why is the latter applicable only to hydrates?
28. List 3 compounds which form hydrates, and 3 compounds which do not.

VI. USES OF WATER (72).

VII. HEAVY WATER (73).

29. Show how heavy hydrogen is a valuable tool in biological research.

**Reading References:** Articles number 12, 17, 58, 75, 117, 410 and 423 in the Appendix.

# PART II: PHYSICAL CHEMISTRY

States of matter; fundamental laws; chemical arithmetic; atomic and molecular weights; solutions; ionization; energy; equilibrium; oxidation and reduction; acids and bases; atomic structure

Together with two chapters on common table salt, illustrating the chemistry of metals, non-metals, acids, hydroxides, and salts

## CHAPTER VIII

## STATES OF MATTER

**74. Matter.**—Matter may be defined as anything which possesses weight or mass. Matter occupies space. Matter exists in three different states,—the **solid**, the **liquid**, and the **gaseous.** These states of matter depend upon temperature and pressure. Thus, water exists as ice, liquid, and vapor. At 0° C., liquid water freezes, or ice melts to form a liquid; 0° C. is therefore the fusion point of ice, or its melting point. If heat is supplied to water at 100° C., under 760 mm. of pressure (nearly 30 inches of mercury), it boils, *i.e.*, gives off vapor (steam) freely.

In fact, most substances have been prepared in these three states: gaseous, liquid, and solid. We shall now consider each one.

### THE GASEOUS STATE

**75. Measurement of the Quantity of a Gas.**—In stating the amount of any gas, it is not sufficient to say that we have so many liters of the gas. We must also specify the temperature and pressure at the time of measuring the gas. This is because the volume of a gas varies considerably as the temperature and pressure are changed. Solids and liquids, on the other hand, are much less sensitive to pressure and temperature.

**76. Measurement of the Pressure of a Gas.**—The pressure of a gas is most accurately and easily measured by an indirect method: a gas is brought exactly to the same pressure as the surrounding atmosphere and then the atmospheric pressure is measured with a **barometer** (Greek, meaning *weight-measurer*).

### DEMONSTRATION 31. A BAROMETER

**Materials: 100 cm. length of 10 mm. tubing sealed at one end, mercury, 50 mm. crystallizing dish half full of mercury, ring stand, clamp, meter stick.**

Fill the tube with mercury, cover with the thumb, invert and lower the open end into the mercury in the crystallizing dish. When the thumb is removed, the column of mercury sinks and finally comes to rest at a height determined by the pressure of the atmosphere. (Fig. 38.) At sea level this height is about 760 mm. (nearly 30 inches); so that **760 mm. is called standard pressure.** The experiment just outlined was first performed in 1643 by Torricelli, a pupil of Galileo.

### DEMONSTRATION 32. ATMOSPHERIC PRESSURE

Materials: Apparatus shown in Fig. 39 set up to operate.

That the height of the column of mercury depends upon the pressure of the atmosphere may be shown by sucking air out of a bell-jar surrounding the lower part of a barometer. The barometric column falls, of course, as the air pressure diminishes. This important fact was known to Robert Boyle in 1659, shortly after the air-pump was invented by Otto von Guericke.

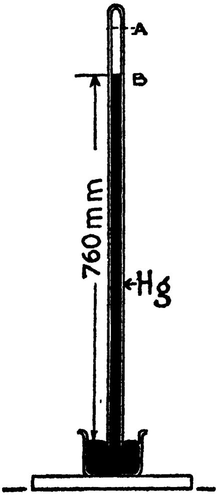


FIG. 38.

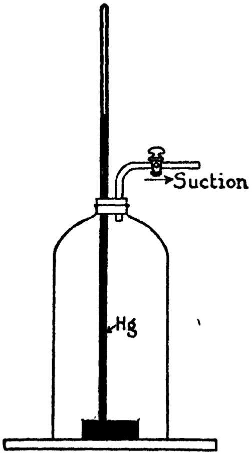


FIG. 39.

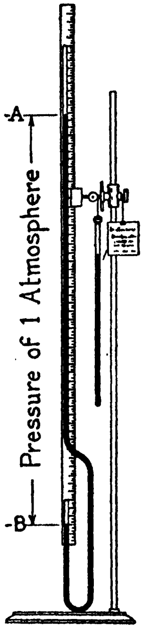
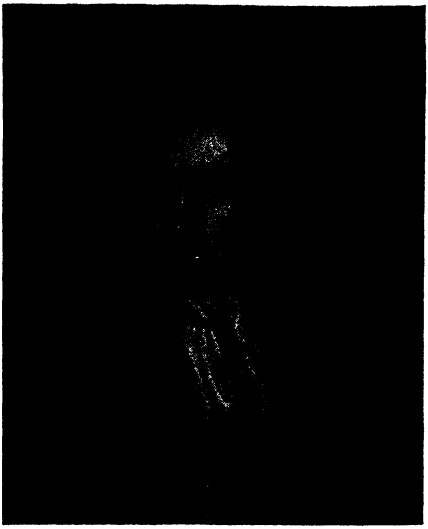


FIG. 40.

Pascal carried out a number of experiments to ascertain if it were really the pressure of the atmosphere which sustained the



ROBERT BOYLE (1626–1691)

Boyle was a son of the Earl of Cork. He was a broadly educated man whose life was devoted to science. Boyle was the first chemist clearly to define the term "element" and to use the term "chemical analysis" in its modern sense. He was president of the Royal Society, 1680–1691.

JACQUES CHARLES (1746–1823)

Charles, a French mathematician and physicist, was the first to employ hydrogen in balloons. About 1787 he discovered that when a gas is heated, it expands 1/273rd of its volume at 0° for each degree rise in temperature (Charles' law). He devised many ingenious physical instruments, and published numerous mathematical papers. Elected to the Academy of Sciences in 1785, he became professor at the Conservatoire des Arts et Metiérs.

column of mercury. He discovered that the barometric column was shorter at higher altitudes; also, that the length of the column depended upon the density of the liquid used: *e.g.*, for mercury at sea level it was about 30 in., and for water, 34 ft. Mercury is 13.595 times as heavy as water, so this fact accounts for the difference.

The barometer commonly employed in the laboratory consists of a U-tube closed and evacuated at one end. The vertical height of the column of mercury from the two mercury surfaces measures the pressure of the atmosphere (A to B in Fig. 40). A correction for the expansion of mercury must be made. A column of mercury at 20°, for example, is 2.6 mm. longer than it would be at 0°; 2.6 mm. must therefore be subtracted from the height of the mercury column. See Appendix, Table IV.

In order to find the **volume of a gas** under atmospheric pressure, the vessel containing the gas is inverted in a vessel containing a liquid, usually mercury or water. The surface is adjusted as at A, Fig. 41, and the volume read. In B the gas is under less than atmospheric pressure; in C it is under more.

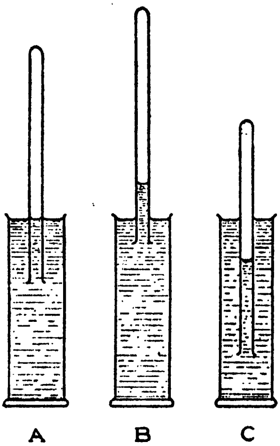


FIG. 41. Measuring a gas. The meniscus should be at position *A*.

**77. Variation in the Atmospheric Pressure.**—The pressure of the atmosphere varies greatly from time to time, so it is necessary to select some pressure known as a standard (normal) pressure. **This standard pressure is 760 mm. of mercury measured at 0°C.** This is equal to 29.9217 in.

To show the variation of pressure at Princeton, it is of interest to know that on January 19, 1904, it was 782 mm. and on January 10, 1940, 720 mm.—a difference of 62 mm.

At 720 mm. water boils at 98.72°, and at 782 mm. its boiling point is 100.8°—a difference of 2.08°.

The normal pressure of the atmosphere per sq. cm. of surface is 1033.2 g. (76 × 13.595. Why?). A sq. in. of surface is exposed to a pressure of approximately 15 pounds, and the pressure supported on the body of the average man amounts to about 18 tons!

**78. Correction of Volume to Standard Pressure.**—Robert Boyle (1626–1691), a brilliant Irish chemist, enunciated (1660) a law governing the change in volumes of gases with change in pressure. **Boyle's Law** may be stated thus:

**The temperature remaining constant, the volume of a given mass of a gas is inversely proportional to the pressure to which it is subjected.** This law may be stated mathematically as follows:

$$\frac{p_1}{p_0} = \frac{v_0}{v_1},$$

whence $$p_1v_1 = p_0v_0.$$

The pressure ($p$) multiplied by the volume ($v$) of a given mass of a gas at a fixed temperature is constant:

$$pv = \text{constant}.$$

This law means that if the pressure applied to a gas is doubled, the volume is halved, etc. Any change in volume due to a change in pressure may be made by a simple direct application of the law.

*Example.*—25 cc. of hydrogen gas is collected under a pressure of 775 mm Find the volume under 760 mm. of mercury.

Since the pressure of gas is lowered, the volume must become larger; hence we multiply by a fraction larger than unity:

$$v = 25 \times \frac{775}{760} = 25.5 \text{ cc.} \quad \text{ANS.}$$

**79. Measurement of Temperatures.**—There are three common temperature scales:

(1) The Fahrenheit Scale, F.° (Not used in scientific work.)
(2) The Centigrade Scale, C.°
(3) The Absolute (Kelvin) Scale, A.°

On the Fahrenheit scale, ice melts at 32° and water boils at 212° (under standard atmospheric pressure)—a difference of 180°. The corresponding points on the Centigrade scale are 0° and 100° —a difference of 100°. It follows, therefore, that

$$1° \text{ F.} = \frac{100}{180} \text{ of } 1° \text{ C., or } \frac{5}{9} \text{ of } 1° \text{ C.}$$

The following formulae can be used for converting one temperature to the other:

$$\text{F.}° = (9\text{C.}°/5) + 32°; \text{ and C.}° = (\text{F.}° - 32°)5/9.$$

*Problem.*—Convert 21° C. to the Fahrenheit scale. Convert 90° F. to the Centigrade scale.

The **absolute scale** of temperature is based upon the fact that the volume of a given mass of a gas, the pressure remaining constant, will increase or decrease 1/273 of its volume at 0° C. for every degree through which it is heated or cooled. The zero point on this scale is −273° C., and is called the **absolute zero.** 273° A. is the same as 0° C. It follows, therefore, that A.° = C.° + 273. A temperature of 20° C. = 293° A. In the correction of the volume of a gas for temperature, C.° must always be converted to A.°.

The accompanying diagram (Fig. 42) shows the relation of the temperature scales to each other, and the relation of the volumes of gases to the absolute temperature.

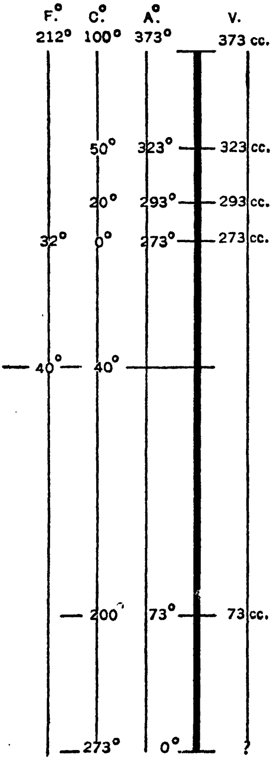


Fig. 42. Temperature scales and corresponding volumes.

An examination of the diagram shows that a gas should have no volume at absolute zero, but as a matter of fact all known gases are liquid or solid before this temperature is reached. Helium is the most difficult of the gases to liquefy. Liquid helium boils at 4.5° A., or −268.5° C. By the rapid evaporation of the liquid a temperature below 1° A. has been reached.

**80. Correction of Volume to Standard Temperature.**—In carrying out chemical calculations involving the volumes of gases, a standard temperature is always used. This **standard temperature is 0° C.** The volume of a gas at one temperature may be changed to its volume at 0° C. by applying the **Law of Charles**[1] (1787): **the pressure remaining constant, the volume of a given mass of a gas is directly proportional to the absolute temperature.**

At constant pressure,

$$v \propto T.$$

---

[1] The law of Charles was discovered independently by Dalton in 1801 and by Gay-Lussac in 1802. The experiments of Charles were not published, but were communicated verbally to Gay-Lussac.

The law may be stated mathematically thus:

$$\frac{v_0}{v_1} = \frac{T_0}{T_1}.$$

In this expression $v_0$ is the volume of a given mass of gas at zero degrees centigrade (where $T_0 = 273°$ Absolute); $v_1$ is the volume at the absolute temperature $T_1 (= 273° + C.°)$.

We have seen that all gases, when heated or cooled under constant pressure, expand or contract by an equal fraction of their volume at 0° C. for equal changes in temperature. The coefficient of expansion is 1/273 for a change of 1° C.

Any change in volume of gas produced by change in temperature may be made by a direct application of the law of Charles.

*Example.*—10 cc. of hydrogen is collected at 20° C. Find the volume at standard temperature (0° C. = 273° A.).

$$v_0 = 10 \times \frac{273}{(273 + 20)} = 9.32 \text{ cc. ANS.}$$

We multiply by a fraction less than unity, for the gas cools down from 293° A. to 273° A.

**81. Correction of Volume to Standard Temperature and Pressure (S.T.P.).**—Any change of volume produced by a change of pressure and temperature may be made by a simple direct application of the two laws.

*Example.*—25 cc. of nitrogen is collected at 21° C. and under a pressure of 750 mm. Find the volume at S.T.P.

$$V_{\text{S.T.P.}} = 25 \times \frac{273}{294} \times \frac{750}{760} = 23.0 \text{ cc. ANS.}$$

Carefully inspect each fraction before making the calculation and see that it produces a change in the desired direction. If the desired temperature is lower, the volume must decrease; if the desired pressure is lower, the volume must increase.

State the conditions when the desired temperature is higher than the observed; when the desired pressure is greater than the observed.

*Note:* Another method of making these calculations is by use of the equation

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2},$$

where $p_1$, $v_1$ and $T_1$ are the initial conditions, and $p_2$, $v_2$ and $T_2$ are the final conditions; it being remembered that $T_1$ and $T_2$ are expressed in degrees absolute.

If the student is to employ this equation, he should first construct a table of values as illustrated by solving the example given above.

| | $p$ | $v$ | $T$ |
|---|---|---|---|
| initial | 750 mm. | 25 cc. | 294° A. |
| final | 760 mm. | $V_{\text{S.T.P.}}$ | 273° A. |

Whence the equation becomes

$$\frac{750 \times 25 \text{ cc.}}{294} = \frac{760 \times V_{\text{S.T.P.}}}{273}$$

which rearranges to the same solution as is given above.

**82. Mixed Gases. Dalton's Law.**—In our discussion of the effect of temperature and pressure upon the volume of a gas, we said nothing about the chemical composition of the gas. From this, the student would infer that mixtures of gases, provided they did not react chemically, would behave exactly like a single gaseous substance. This fact was enunciated by Dalton in 1807 as follows:

**A mixture of gases, provided they do not combine chemically, exerts a pressure equal to the sum of the pressures which would be exerted by each of the components separately if allowed to fill the containing vessel alone at the particular temperature.**

In other words, the pressure exerted by one gas does not interfere with the pressure exerted by another; they are independent of each other. The pressure exerted by each gas is called its **partial pressure,** and the partial pressure is proportional to the concentration of the particular gas in the mixture.

The student may not at first grasp the fundamental importance of this law. Actually, most of our gases are collected and measured over water. Since we have already seen (67) that there is always water vapor above the surface of water, this means that the gas we are measuring contains water vapor; that is, it is a *mixture* of gases. The quantity of water present as gas is given in Table 15, and is greater the higher the temperature. The partial pressure of the water vapor is called aqueous tension, or the **vapor pressure of water.**

The presence of moisture in a gas makes its volume larger than the volume of the dry gas, so in order to reduce the volume of a gas, measured over water, to the dry condition, *the aqueous tension is subtracted from the corrected barometric pressure.*

*Example.*—25 cc. of oxygen, measured over water at 20° C. and under a pressure (corrected) of 765 mm., would occupy what volume when reduced to the dry condition and to S.T.P.?

*Note.*—The aqueous tension at 20° C. = 17.4 mm.

$$V_{\text{S.T.P.}} = 25 \times \frac{273}{293} \times \frac{(765 - 17.4)}{760}.$$

**83. Deviations from the Gas Laws.**—While the laws of Boyle and of Charles are close approximations to the behavior of gases, most gases deviate to a slight extent from the so-called **perfect gas.**

Deviation from Boyle's law for several gases is shown in Table 17. Two liters of gas at 1 atmosphere pressure and 0° C. were compressed to 2 atmospheres pressure; and the resulting volume is given in the second column of the table. With the exception of hydrogen and helium, all gases are more compressible at moderate pressures, and less compressible at high pressures than Boyle's law would lead one to expect.

Deviation from Charles' (Gay-Lussac's) law is shown in the third column of Table 17 for expansion from 0° to 100° at 760 mm. pressure. Here the coefficient of thermal expansion according to Charles' law should be 1/273, which is 0.00366. Gases which liquefy easily deviate most from the law. The reason for this deviation will be explained in section 97.

TABLE 17. DEVIATIONS FROM GAS LAWS

| Gas | Boyle's | Charles' (Gay-Lussac's) |
|---|---|---|
| Perfect gas | 1.0000 liters | 0.003661 |
| Ammonia | 0.9845 | 0.003770 |
| Carbon dioxide | 0.9931 | 0.003726 |
| Hydrogen | 1.0006 | 0.003664 |
| Oxygen | 0.9995 | 0.003672 |
| Sulfur dioxide | 0.9739 | 0.003845 |

**84. Diffusion of Gases. Graham's Law.**—When a cylinder containing hydrogen is placed mouth downward above another cylinder containing air, the particles of hydrogen, despite their lightness, move downward and penetrate the air, and the air moves upward and penetrates the hydrogen. This movement of the gases goes on until a homogeneous mixture is obtained. The molecules of gases possess independent power of locomotion. The phenomenon is known as **diffusion.**

### DEMONSTRATION 33. DIFFUSION OF HYDROGEN

Materials: Set-ups in Fig. 43. Porous clay cups fitted with one-holed rubber stoppers. Leads from U-tube are connected with a dry cell and electric door-bell. Two liter beakers. Tank of hydrogen.

If the large beaker is filled with hydrogen and lowered over the porous cup, hydrogen diffuses into the cup more rapidly than the slower moving air diffuses out. This increases the pressure in the tube causing (a) a fountain or (b) the mercury to rise in the U-tube, completing the circuit and ringing the door-bell.

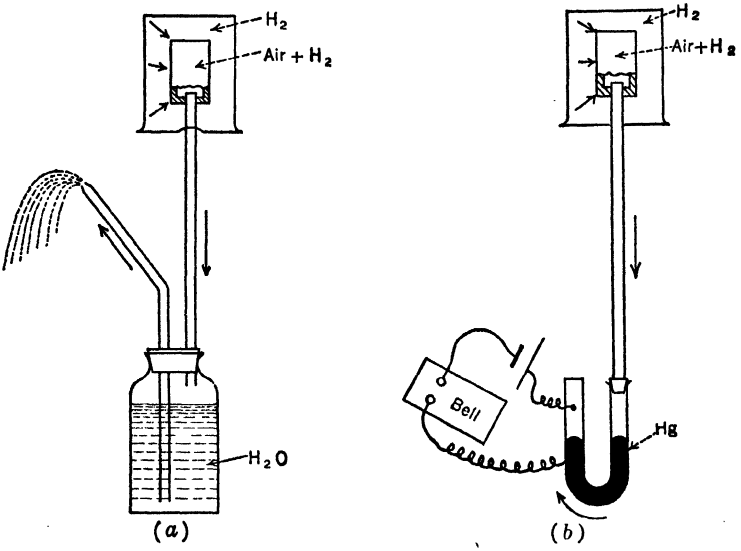


FIG. 43. Diffusion of gases: (a) fountain; (b) rising mercury rings bell.

**Graham** (1833) enunciated a law governing the rates of diffusion (r) of gases in relation to their densities (d): **the rate or speed of diffusion of a gas is inversely proportional to the square root of its density:**

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}}.$$

Thus hydrogen (molecular weight 2) diffuses four times faster than oxygen (molecular weight 32) since

$$\frac{r_{H_2}}{r_{O_2}} = \frac{\sqrt{32}}{\sqrt{2}} = \sqrt{\frac{16}{1}} = 4.$$

Other gases behave similarly. We detect the delicate odors of perfume because molecules of the perfume have diffused to our nostrils; the evil smell of hydrogen sulfide associated with chemistry comes from the diffusion of that gas out of the analytical laboratory, where it is in constant use, into the lecture room, where we suffer its abuse. Owing to diffusion the composition of the atmosphere is practically constant for many miles above the surface of the earth: if it were not so, our earth would be encircled by concentric shells of carbon dioxide, oxygen, nitrogen, water vapor, and other gases.

## THE LIQUID STATE

**85. The Liquefaction of Gases.**—We have already learned that all gases will liquefy if proper temperature and pressure are used, but that a gas will not liquefy above its critical temperature no matter how much pressure is applied (34). Critical temperatures and corresponding critical pressures at which liquefaction occurs are given for a few substances in Table 18.

TABLE 18. CRITICAL TEMPERATURE AND PRESSURE

| Gas | Critical temperature in ° C. | Critical pressure in atmospheres |
|---|---|---|
| Ammonia | +132.4 | 112 |
| Carbon dioxide | + 31.35 | 72.85 |
| Chlorine | +144.0 | 76 |
| Helium | −267.9 | 2.26 |
| Hydrogen | −239.9 | 12.8 |
| Nitrogen | −147.1 | 33.5 |
| Oxygen | −118.8 | 49.7 |

In Chapter VII we learned that water boils at 100° C. because its aqueous tension becomes 760 mm., the pressure of the atmosphere, at that temperature. In the same way for other liquids, their vapor pressures at their boiling points are 760 mm. The boiling points of some liquids are given in Table 19. All liquids release gaseous vapor to the space above them; and in a closed vessel equilibrium is reached, with a definite vapor pressure for each temperature.

**86. Heats of Vaporization and of Fusion.**—Approximately 540 calories of heat are consumed in coverting 1 gram of water at 100° C. from water into steam; and 80 calories are given off in freezing it. Other liquids exhibit characteristic heats of vaporization and of fusion (melting). Some of these are tabulated below.

TABLE 19. HEATS OF VAPORIZATION AND OF FUSION

| | B.P. | M.P. | Heats in cals. per g. | |
|---|---|---|---|---|
| | | | Vaporization | Fusion |
| Benzene | 80.2° | 5.5° | 92.9 | 30 |
| Carbon dioxide | −78.5° | sublimes at −55.6° | 72.23 at −25° | 43.2 |
| Water | 100° | 0° | 539 | 79.77 |

**87. Viscosity.**—The attractive forces between the molecules of a liquid set up a resistance to flow which is called **viscosity**. At one extreme we have substances which flow readily, such as water or ether; at the other, we have substances with high viscosity, such as molasses and tar. Even glass is not a solid, but a super-cooled liquid, for it has no sharp melting point. The problem of keeping lubricating oils freely flowing even at low temperatures is largely a question involving viscosity. Viscosity is measured by the rate of flow of the liquid through a capillary (from $x$ to $y$, Fig. 44), or by the rate of fall of a steel ball through the liquid, or by the number of revolutions which vanes, discs or cylinders describe in the liquid after the motor driving them has been disconnected.

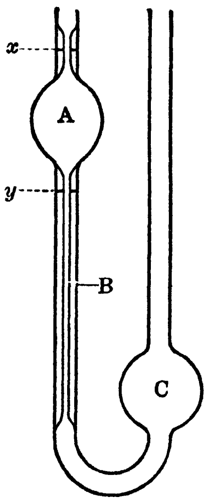


FIG. 44. Ostwald viscosimeter.

**88. Surface Tension.**—While the molecules inside a drop of water are being attracted by its neighbors *equally in all directions*, the molecules on the surface of the drop are being attracted only *inwards*. This inward attraction is called **surface tension.** The drop assumes that shape which will reduce this tension to a minimum, which in this instance is a sphere. This same force raises water above the normal level in a capillary tube; and the liquid in the tube forms a concave surface, called a **meniscus**. For liquids which do not wet glass, such as mercury, the meniscus is convex. In this case the glass has no attraction for the mercury; instead the molecules are pulled away from the glass by mercury molecules within the body of the mercury, tending to form a sphere, which is convex.

**89. Solution Versus Liquid.**—A pure liquid should be distinguished in the student's mind from a solution. In the latter, two or more substances may be dissolved in one another. These substances may be gaseous, liquid or solid, viz. carbon dioxide in water, table salt in water, alcohol in water, lead in silver. The chemist is interested in the physical properties of these solutions, too, such as boiling point, freezing point, vapor pressure, surface tension and viscosity. Most of the liquids the student sees about the laboratory are water solutions of different solid substances. A few are pure liquids, *e.g.*, alcohol, benzene, chloroform, ether, carbon tetrachloride and carbon disulfide. These latter, if pure, contain no water at all; they are not solutions.

## THE SOLID STATE

**90. Amorphous and Crystalline Solids.**—Solids may be divided into two classes, amorphous and crystalline. In **amorphous solids** the arrangement of the particles is chaotic, *i.e.*, not arranged according to a definite pattern. The arrangement of the particles may be likened to trees growing in a natural forest. In a **crystalline substance**, on the other hand, the particles are arranged in definite order, like trees in a nursery or garden, or soldiers on parade.

Crystals have a structure, and therefore many of them possess marked cleavage, as illustrated in mica. This mineral may be split into sheets of inconceivable thinness; indeed, it is estimated that a single sheet may be only two molecules in thickness!

While some crystals are microscopic, others are very large. A natural crystal was found which measured 3 feet by 6 feet by 42 feet in length; 37 tons of spodumene (lithium aluminum metasilicate) having been quarried from this single crystal. Artificial crystals do not reach these dimensions, but very long metallic crystals have been prepared. Thus, when plastic tungsten is drawn through a die at such a rate that the particles have time to arrange themselves in definite order, crystals a mile or more in length may be prepared.

A **crystal** may be defined as a substance bounded by plane faces at definite angles to each other and having physical properties alike along parallel directions. Crystals are formed by the solidification of a substance—elementary or compound—or by the deposition of a substance from solution. The smallest crystal which makes its appearance has the same crystalline form as a large crystal. Crystals are formed, therefore, by growth.

### DEMONSTRATION 34. A SILVER TREE

Materials: Silver nitrate solution, fine copper wire, watch glass.

When a very fine wire is placed in a few drops of silver nitrate solution, small crystals of silver, the so-called "silver tree," are formed.

**91. Classification of Crystalline Forms.**—Notwithstanding the large number of crystalline forms, all crystals may be classified in seven systems. These systems are readily defined by referring each to fundamental axes. They are as follows:

**I. Regular Cubic (Isometric) System**

Three equal and interchangeable axes at right angles. NaCl, $FeS_2$, PbS, etc., belong to this system; also most metals. (Fig. 45–I.)

**II. Square Prismatic (Tetragonal) System**

Three axes, all at right angles, two of which (the lateral axes) are interchangeable and equal: *e.g.*, zircon ($ZrSiO_4$), nickel sulfate ($NiSO_4, 6H_2O$), tin oxide, $SnO_2$. (Fig. 45–II.)

**III. Hexagonal System**

Four axes, three of which are equal and interchangeable, being in the same plane and at an angle of 60° to one another. All are at 90° to the fourth axis: *e.g.*, $SiO_2$ (quartz). (Fig. 45–III.)

**IV. Rhombic (Orthorhombic) System**

Three unequal axes, all at right angles: *e.g.*, $KMnO_4$, $KNO_3$, $\alpha$-sulfur, topaz. (Fig. 45–IV.)

**V. Monosymmetric (Monoclinic) System**

Three axes, all unequal, two of which (the lateral) are at right angles. One of these is at right angles to the third or C axis; the other is inclined: *e.g.* feldspar, rock candy, tartaric acid, $\beta$-sulfur. (Fig. 45–V.)

**VI. Asymmetric (Triclinic) System**

Three axes, all unequal and inclined: *e.g.*, copper sulfate ($CuSO_4, 5H_2O$). (Fig. 45–VI.)

**VII. Rhombohedral (Trigonal) System**

Three axes equally inclined, not all at right angles; all equal: *e.g.*, $CaCO_3$ (calcite) As, Sb, ice. (Fig. 45–VII.)

**92. Methods for Studying the Internal Structure of Crystals.**—Two different effects are utilized: diffraction and reflection.

### a. Diffraction patterns.

When visible light is passed through a prism, a color spectrum is produced. A similar spectrum is produced if the light is shone upon a **diffraction grating,** a metal strip upon which as many as 25,000 lines to the inch have been scratched. The distance apart of these lines must be about the same as the wave-length of the light used.

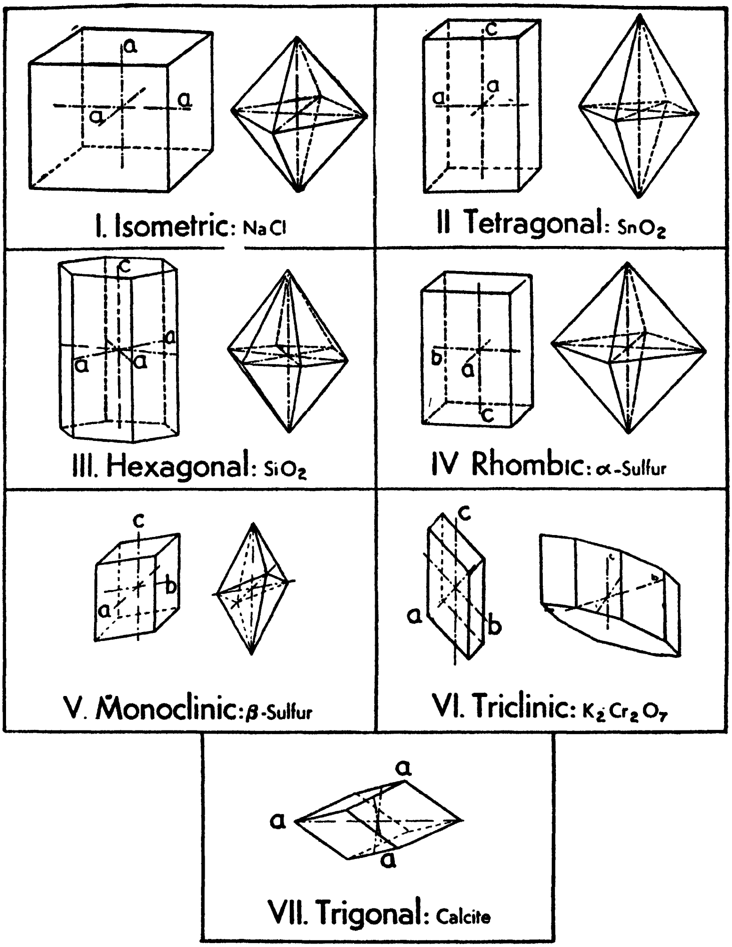
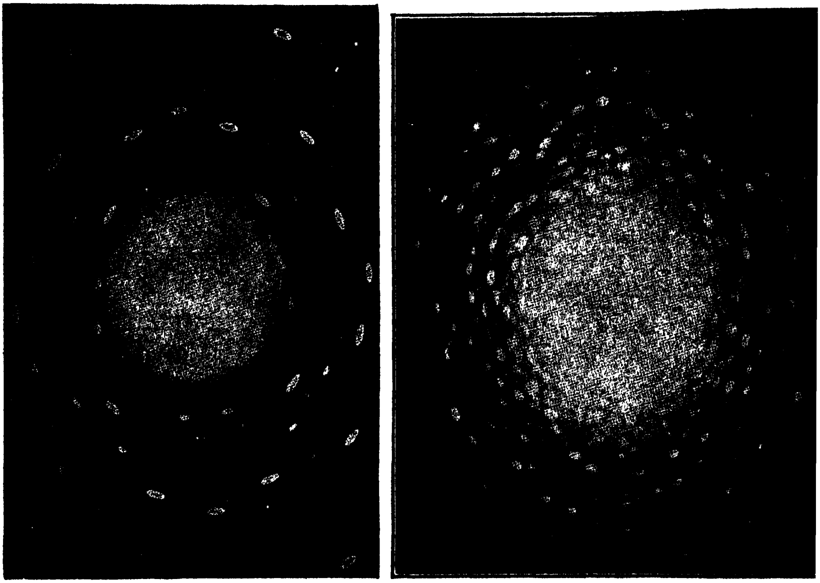


FIG. 45. Crystal systems.

Now X-rays are light with a wave length a hundred to a thousand times shorter than visible light. The distances between lines on a metal diffraction grating would therefore be too great to get spectra with X-rays. In 1912 it occurred to von Laue of the University of Zurich that successive rows of particles in a crystal were sufficiently close to act as a diffraction grating for X-rays. Von Laue's conclusion has been fully confirmed by experiment, and his technique employed in studying the structure of crystals. When **a beam of X-rays is passed through a thin section of a crystal** and then allowed to strike a photographic plate, a diffraction pattern of the crystal lattice is produced (Fig. 46). Laue made photographs of sodium nitrate, anhydrite, aragonite, potash alum (Fig. 46) and so forth. From the position of the crystal, its distance from the photographic plate, and its



Laue Photograph of Magnesium Oxide

Laue Photograph of Potash Alum

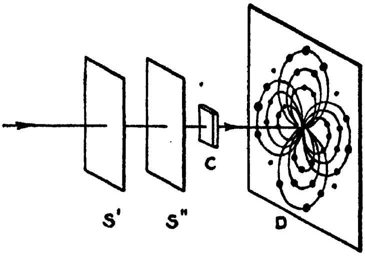


FIG. 46. Laue diffraction patterns. $S'$, $S''$ slits; $C$ crystal; $D$ photographic plate. Above, actual photographs.

crystallographic measurements, physical chemists are able to construct models of the space lattice of crystals.

Debye and Scheerer (1916) and Hull (1917) independently devised a method which employed the substance in the form of a fine powder consisting of tiny crystals. **A beam of X-rays is passed through the powdered crystals,** the rays being diffracted to a photographic plate, and produce lines for each kind of plane within the crystal. The crystal structure is calculated from the positions and intensities of these lines.

### b. Reflection patterns.

Bragg and Bragg (1913) used a different device for studying crystal structure with X-rays. When **X-rays are shot against the surface of a crystal** the beam is intensified wherever it is reflected from several atoms. Thus in Fig. 47 it is seen that the X-ray beam is intensified along line $A$-$B$-$C$-$N$ since there is reflection of this beam from atoms $A$, $B$, and $C$. A photographic plate placed in the path of the reflected X-ray would show a dark spot at point $N$. From a pattern of such spots, the physical chemist is able to determine the relative positions of the atoms in the space lattice of the crystal. They can measure the distances between the rows of particles within the crystal. Such a picture for sodium chloride is shown in Fig. 49. **The structure of the crystal depends upon the arrangement of the constituent atoms or ions and not upon that of the molecules.** The atoms, or ions, are the units that give the crystallographic patterns.

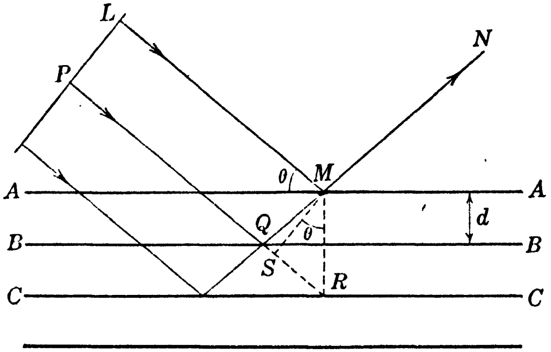


FIG. 47. X-ray reflection from equidistant planes (Bragg and Bragg).

**93. Lattice Structure of Crystals.**—The X-ray method has demonstrated a number of lattices. The simplest lattice is the

**simple cubic lattice**, which is the most symmetrical arrangement possible, and the arrangement generally present in those substances which crystallize in the regular, isometric system **(91)**. Three sub-types of the cubic lattice are shown in Fig. 48.

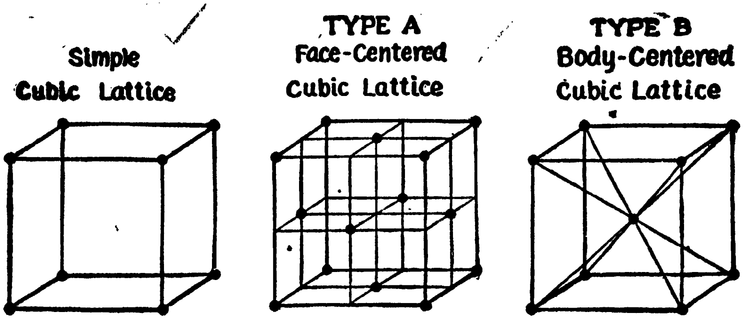


FIG. 48. Cubic lattices.

**Sodium chloride** assumes the simple cubic lattice. An exact picture of this substance is shown in Fig. 49. The student will

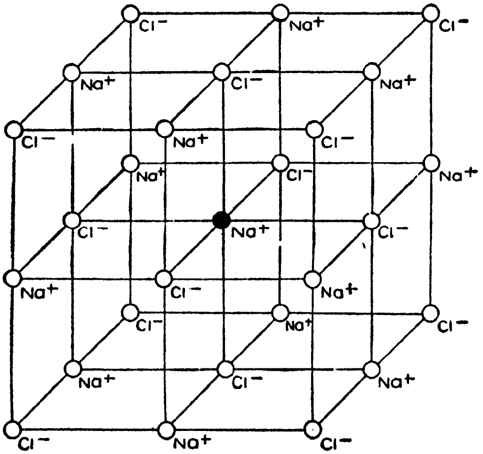


FIG. 49. The sodium chloride lattice. Actually, the ions are much larger than is represented, probably in contact with one another.

at once notice that the atoms have lost or gained electrons, to become *ions* in a crystal of sodium chloride. The bonds which hold these ions together are called **polar bonds**. Each sodium ion is equidistant from six chloride ions and in the same way, each chloride ion is surrounded by, and equidistant from, six sodium ions. The term *molecule* loses its significance when applied to this crystal, then, for it is impossible to pair off any particular sodium ion with a chloride ion in Fig. 49. Potassium chloride, magnesium oxide, and calcium sulfide are similar in structure to sodium chloride.

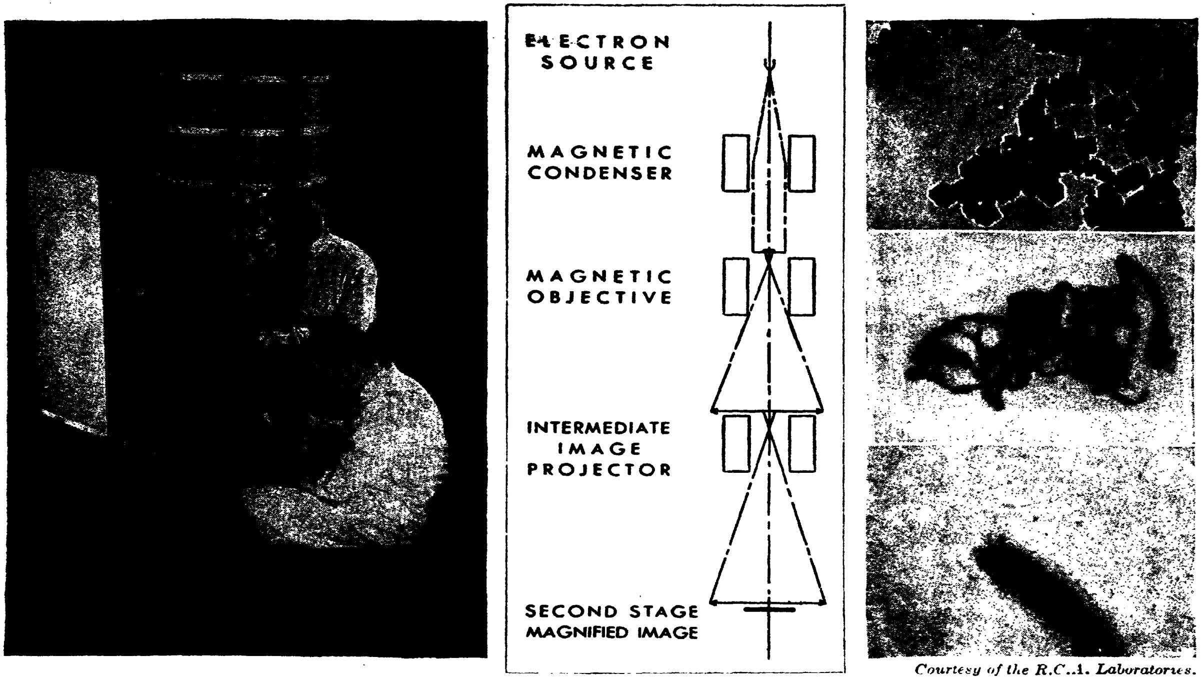
A second cubic lattice is the **face-centered cubic lattice**, exhibited by copper, silver, gold, aluminum, nickel and platinum. The third type is the **body-centered cubic lattice**, represented by sodium, potassium, iron, chromium and tungsten. All of these types are illustrated in Fig. 48.

There are, of course, other lattice types of varying complexity. Thus, X-ray analysis shows that the diamond consists of carbon atoms arranged in the form of a tetrahedron, with four atoms at the corners and a fifth atom at the mass-center (Fig. 159).

**94. Electron Diffraction.**—Electrons act both as particles and as light waves. Like visible light, and like X-rays, therefore, they give diffraction patterns. The structure of the molecule of any substance which can be obtained as a gas can be determined by **electron diffraction.** A beam of electrons is shot through the gas, and from the way the electrons are scattered the structure of the molecules can be deduced. The electrons are accelerated by about 50,000 volts, and are recorded on a photographic plate. It has been found, for instance, that chlorine gas consists of $Cl_2$ molecules and that the chlorine atoms are $1.98 \times 10^{-8}$ cms. apart.

Diffraction patterns with electrons have not been very successful in studying atomic distances in solids.

On the other hand electrons in place of visible light are used in a super-microscope developed by the Radio Corporation of America (1939) and Siemens and Halske of Germany. Magnifications a thousand-fold greater than with visible light are possible, so that single molecules, such as giant protein virus molecules, may be photographed. This is because the wave length of an electron beam is nearly a million times shorter than of visible light (visible light 4000–8000 Å, electron beam about 0.01 Å), and the shorter the wave length, the greater the resolving power of the microscope. Research with this **electron microscope** is just in its infancy. Fig. 50 shows some photographs taken with an electron microscope.



*Courtesy of the R.C.A. Laboratories.*

Fig. 50.

***Left:*** First commercial electron microscope.

***Middle:*** The electron microscope focuses electrons with magnetic lenses just as a compound microscope focuses light with glass lenses.

***Right.*** *Upper:* Magnesium oxide × 45,000. *Middle:* So-called "grain" of silver shown to be matted threads rather than a lump. Under the ordinary microscope it appears as a speck (Courtesy of the Kodak Research Laboratories). *Bottom:* Tobacco mosaic virus attached to tip of bacillus. The small dashes are micrographs of individual molecules.

## THE KINETIC THEORY

**95. The Kinetic-Molecular Theory.**—We have seen that there are three states of matter—the solid, the liquid, and the gaseous states. We also have seen that masses are composed of exceedingly small particles called *molecules*, each one of which possesses the same properties as does the mass as a whole; also, that molecules are composed of atoms of elements combined in definite numbers.

It is believed by scientists that the small discrete particles (molecules) of matter are in motion. The energy of motion of molecules is called kinetic, from a Greek word meaning *move;* hence the **Kinetic-Molecular Theory.** In the solid state, the molecules are crowded together so tightly that they lose their identity. We have already seen this to be the case for sodium chloride (**93**) where the crystal is an ordered arrangement of sodium ions and chloride ions, not molecules. In the liquid state there is greater freedom of motion than in the solid state; but there is still a tendency for molecules to associate and move about in clusters. On the other hand, the attractive force between molecules in the gaseous state is practically nil, for the space in which the molecules move is vast when compared with the tiny size of the molecules themselves.

**96. The Kinetic Theory of Gases.**—Since molecules possess a certain mass $m$, and according to the kinetic theory are in motion, let us say with a velocity $v$, they must possess a certain molecular momentum expressed in the classical form $\frac{1}{2}mv^2$. This is called **kinetic energy.** The kinetic theory postulates (1) that at a given temperature the kinetic energy of all gases is the same, and (2) that the kinetic energy of a molecule is directly proportional to its absolute temperature,

$$\tfrac{1}{2}mv^2 = kT.$$

This theory has made it possible to compute magnitudes in the molecular world.

(*1*) *Diameter of molecules.* The diameters of the following molecules are given in Ångstrom units. 1 Å unit is equal to one hundred millionth of a centimeter. $H_2$, 2.72; $CO_2$, 4.6; $N_2$, 3.8; $O_2$, 3.62. Calculate how many million molecules it would take to make a row one inch long!

(*2*) *Number of molecules.* It has been found that there are $2.7 \times 10^{19}$ molecules in 1 cc. of a gas at S.T.P., with a probable error of less than 1 per cent.

(*3*) *Velocity per second.* The velocities of the following gases are: H 1859 meters, or 1.15 miles per second, He 492 meters, O 465 meters, Cl 310 meters. The lighter the molecule the greater its velocity.

(*4*) *Collisions per second.* It has been computed that a hydrogen molecule collides, at S.T.P., with its fellows 9,520,000,000 times per second! At 20° C. (room temperature) the number rises to 10,060,000,000. It would take one individual, counting at the rate of 3 per second 24 hours per day, over a century to count this number.

According to F. W. Aston, if an ordinary electric bulb were evacuated and a minute hole made in its side, just big enough to allow one million molecules to pass per second, it would be 100 million years before the bulb would be filled with air at atmospheric pressure.

According to Sir Oliver Lodge, 250,000,000 atoms in a row would stretch something like an inch, while 100,000 electrons in a row would stretch something like an atom. Also, if the atom were magnified to the size of a cathedral, each constituent electron would be the size of a gnat.

It is particularly instructive to see how the concepts of the kinetic-molecular theory substantiate our observations of the properties of gases. A table is constructed below to emphasize this.

| *Observed Behaviour of Gases* | *Kinetic-Molecular Explanation* |
|---|---|
| (*1*) A gaseous body is homogeneous. | (*1*) The molecules of a gas are closely alike. |
| (*2*) A gas is very compressible. | (*2*). The molecules are relatively far apart. |
| (*3*) Gases diffuse rapidly. | (*3*) The molecules are in rapid motion. |
| (*4*) A gas exerts a pressure on the sides of the containing vessel. | (*4*) Pressure is caused by impact of molecules. |
| (*5*) A gas does not settle appreciably. | (*5*) The molecules are in rapid motion and suffer perfectly elastic collisions. |
| (*6*) Boyle's law.<br>(Volume varies inversely as the pressure.) | (*6*) Decreasing volume ($V$) of the container increases the number of molecules per unit volume, thereby increasing the number of collisions (pressure, $P$) on the wall. ($V = k/P$.) (Fig. 51.) |
| (*7*) Charles' law.<br>(Volume varies directly as the temperature.) | (*7*) Since in $\frac{1}{2}mv^2 = kT$, the only variables for a molecule of given mass $m$ are $v$ and $T$, the velocity of molecular motion, $v$, must vary directly as the temperature, $T$. Increasing temperature increases molecular motion, which increases pressure. The pressure can be kept constant by increasing volume. |

| | |
|---|---|
| (*8*) Graham's law.<br>(Rate of diffusion is inversely proportional to the square root of the masses.) | (*8*) At a given temperature the kinetic energy of all gases is the same. Therefore $\frac{1}{2}m_1v_1^2 = \frac{1}{2}m_2v_2^2$.<br>Rearrangement gives Graham's law: $\frac{v_1}{v_2} = \frac{\sqrt{m_2}}{\sqrt{m_1}}$. |
| (*9*) Dalton's law. | (*9*) Kinetic energy and its variation with temperature is the same for all gases. Mixed gases will therefore exhibit the same $p$, $v$, $t$ relationships as single gases. |
| (*10*) Avogadro's law.<br>**Equal volumes of different gases at the same temperature and pressure contain the same number of molecules.** | (*10*) The expression $pv = \frac{1}{2}nmv^2$, where $n$ is the number of molecules, holds for all gases. If we have equal volumes of gases 1 and 2 at the same pressure, $p_1v_1 = p_2v_2$, and $\frac{1}{2}n_1m_1v_1^2 = \frac{1}{2}n_2m_2v_2^2$. Since, according to the kinetic theory, $\frac{1}{2}m_1v_1^2 = \frac{1}{2}m_2v_2^2$, we have $n_1 = n_2$. |

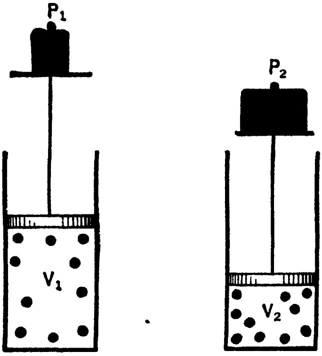


FIG. 51. Boyle's law. Variation of volume with pressure.

The use of the kinetic theory to substantiate Avogadro's law is especially interesting. The fact that a given volume of hydrogen contains no more molecules than an equal volume of oxygen, despite the difference in the sizes of these molecules, is at first puzzling. But since at any given temperature $\frac{1}{2}m_{O_2}v_{O_2}^2 = \frac{1}{2}m_{H_2}v_{H_2}^2$, the hydrogen deficiency in mass, $m_{H_2}$, is made up by an increased mobility, $v_{H_2}$, of the hydrogen molecule. Although Avogadro postulated this important concept in 1811, it received little attention until 1858, at which time Cannizzaro emphasized its usefulness in the calculation of molecular weights (**115**). Since then Avogadro's *hypothesis* has been tested so severely that it is now called a *law*.

**97. Deviations from the Gas Laws.**—The perfect gas should obey the relation

$$pv = kT \quad \text{(ideal gas).}$$

It was seen in section 83, however, that there are considerable deviations from the ideal. These deviations are greatest at high pressures and low temperatures, *i.e.*, when the molecules are forced closely together. An attempt to correct for this deviation was made by Van der Waals (1873) who suggested the equation

$$(p + f)(v - b) = kT, \quad \begin{cases} \text{Van der Waals' equation} \\ \text{of state in which } f = a/v^2. \end{cases}$$

The observed pressure, $p$, is augmented by a force, $f$, which corrects for the fact that molecules just striking the surface of the vessel are attracted unequally by molecules in the gas space. The volume, $v$, has been reduced by the constant, $b$, which represents the space occupied by the molecules themselves, space which is not available for the kinetic motion of other particles. Each different molecule has characteristic constants for $f$ (really for $a$ in an expression $f = a/v^2$), and for $b$; and when these values are inserted in the equation of state, remarkable regularity in the $p$, $v$, $T$ relationships is observed.

**98. The Kinetic Theory of Liquids.**—When a gas is cooled, the speed of the molecules is lowered; and if the temperature is low enough and the pressure great enough to bring the molecules sufficiently close together, they will cohere and form a liquid. Thus oxygen liquefies at −118.8°, the pressure being 49.7 atmospheres; and carbon dioxide, at 31.35°, when under a pressure of 72.85 atmospheres (C.T. and C.P.).

Because there is this greater coherence in liquids, **diffusion of liquids** proceeds slowly as compared with that of gases.

DEMONSTRATION 35. DIFFUSION

Materials: Potassium permanganate crystal fastened to clock-glass by means of wax. Tall cylinder filled to the very top with water.

Upon placing the clock-glass so that the potassium permanganate is immersed in the water, the permanganate gradually dissolves, the solution sinks, and diffusion begins. The process of diffusion proceeds rather slowly until a homogeneous liquid is finally obtained.

**Evaporation** is another manifestation of kinetic motion in liquids. While there is a mean kinetic energy of all the liquid particles, some particles have more, some less, than this mean. Those coming to the surface with sufficient kinetic energy will break away into the gas space above the liquid, and do not return to the liquid. This is evaporation. A draft hastens evaporation by sweeping the gaseous molecules away from the liquid. Since the molecules with greatest kinetic energy are the ones escaping, and since kinetic energy is heat, the "hotter" molecules are escaping; that is, the temperature of the liquid falls as evaporation proceeds.

Many of the molecules which leave the surface also return to it. That is, evaporation and condensation are occurring simultaneously.

If a mass of liquid, *e.g.*, water, be confined at a constant temperature in a closed vessel as shown in Fig. 33, obviously a state would finally be reached when evaporation and condensation would exactly balance each other, or when the number of molecules leaving the surface of the water is equal to the number returning to the liquid state. Such a condition is known as a **kinetic equilibrium**. Both operations—evaporation and condensation—are still in full sway, but they are going on simultaneously, the one just balancing the other.

**99. The Brownian Movement.**—Robert Brown, a botanist, first observed in 1827 that when a little lycopodium, spores of the club moss, is suspended in water and examined under the microscope, the small particles appear to move in a zigzag path (Fig. 52). The kinetic theory furnishes the explanation of this phenomenon. The movement of the suspended particles is due to bombardment by the surrounding water molecules. Calculations indicate a large probability of unequal bombardment by water molecules of the particle at any given moment, resulting in this random motion. The smaller the particle the more effective the bombardment, the livelier the motion. Although Brown, when he first discovered this peculiar motion, attributed it to living matter, he subsequently found that it was exhibited by dead as well as by living particles in suspension.

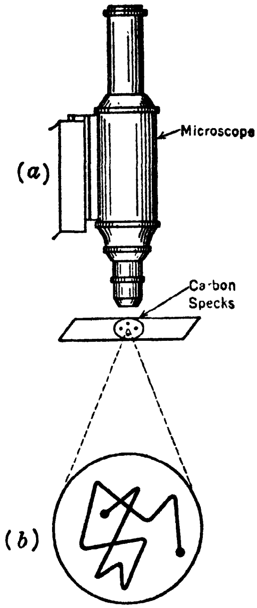


FIG. 52. Brownian movement. (*a*) Arrangement for observing movement. (*b*) Movement of one particle.

### DEMONSTRATION 36. BROWNIAN MOVEMENT

Materials: Microscope, slide, match, mortar and pestle.

A burnt match, well powdered and dusted onto a drop of water on a microscope slide, exhibits lively Brownian movement under a microscope.

Experimental facts in connection with the Brownian movement went far toward establishing the validity of the kinetic-molecular theory.

**100. The Kinetic Theory of Solids.**—A solid body tends to retain the form imposed upon it by nature or by art. Like liquids, solids are characterized by much greater densities than are gases. According to the kinetic theory, a solid body is composed of particles which vibrate in fixed positions. There is mobility even amongst the particles of a solid, however. Thus, when the layer of silver is removed from an old electroplate it will be found that some of the silver has diffused into the copper plate beneath.

Some solids have high vapor pressures similar to those of volatile liquids. Thus camphor, ice, snow, and iodine all evaporate, or **sublime**.

**Reading References:** Articles number 17, 41, 44, 65, 75, 208 and 212 in the Appendix.

## QUESTION REVIEW

STATES OF MATTER (74).

I. THE GASEOUS STATE.

**a. Measurement of the quantity of a gas (75).**

1. What must be specified in stating the amount of a gas? of a liquid? of a solid?

**b. Pressure (76). Atmospheric pressure (77). Correction (78).**

2. Describe the barometer. Why is mercury, rather than water, used in a barometer?
3. What is the boiling point of water when atmospheric pressure is 782 mm.? What is S.T.P.?
4. 35.5 cc. of nitrogen are collected at 740 mm. What would the volume be at 760 mm.? at 755 mm.?
5. Change 20 cc. of gas at 730 mm. and 0° C. to S.T.P.

**c. Temperature (79). Corrections (80–81).**

6. Body temperature is normally 98.6° F. What temperature is this in ° C.?
7. Photographic developing is often carried out at 18° C. What is this temperature in ° F.?
8. A hydrogen balloon containing one cubic foot of gas at 20° C. and 760 mm. will change to what volume when cooled in liquid air to −193° C.?
9. 20 cc. of hydrogen at 24° C. and 750 mm. will have what volume at S.T.P.?
10. Change 36 cc. of gas at 45° F. and 700 mm. to S.T.P.
11. A 200 cc. flask holds 0.2625 g. of oxygen, measured at 17° C. and 742 mm. From these data calculate the weight of 1 cc. of oxygen at S.T.P.

**d. Dalton's law (82). Perfect gas (83). Diffusion (84).**

12. What bearing has Dalton's law in measuring the volume of a gas collected over water?
13. Name the gases in Table 17 which deviate most from a perfect gas. Compare with their boiling points.
14. Consult the table of atomic weights, and calculate the relative diffusibilities of the following pairs of molecules: $H_2$ and $O_2$; CO and $CO_2$; $Cl_2$ and $N_2$; HCl and $H_2S$.

II. THE LIQUID STATE.

**a. The liquefaction of gases (85). Heats of vaporization (86).**

15. Define critical temperature and critical pressure. Which of the following gases can be liquefied at room tempera-

ture: hydrogen, oxygen, carbon dioxide, chlorine, nitrogen?

**b. Viscosity (87). Surface tension (88). Solution (89).**

16. Describe two methods for measuring viscosity.
17. Explain surface tension and viscosity in terms of molecular forces.

### III. THE SOLID STATE.

**a. Amorphous and crystalline (90). Crystalline forms (91).**

18. Name the seven crystal systems. Describe their axes Give one example of each.

**b. Studying crystals (92). Lattices (93). Electrons (94).**

19. Describe, also illustrate, spectrum, diffraction gratings, X-rays, X-ray spectrometer, crystal lattice, polar bond.
20. Describe methods using the X-ray for studying crystal structure. What did each of the following contribute: von Laue, Bragg and Bragg, Hull, Debye and Scherrer?
21. Why is the term *molecule* inappropriate in describing sodium chloride?

### IV. THE KINETIC THEORY (95).

**a. The kinetic theory of gases (96). Deviations (97).**

22. Draw up a table comparing the (a) observed behavior of gases with (b) kinetic-molecular explanation of this.
23. State Avogadro's law. Derive it mathematically from the kinetic expression $pv = \frac{1}{3}nmv^2$.
24. Explain the physical significance of the constants $f$ and $a$ in Van der Waal's equation of state.

**b. The kinetic theory of liquids (98). Brownian movement (99).**

25. Explain liquefaction and evaporation in terms of the kinetic theory. Why does the temperature of a liquid fall as evaporation proceeds?
26. Explain Brownian movement in terms of the kinetic-molecular theory.

**c. The kinetic theory of solids (100).**

27. Describe an experiment proving that the molecules of solids are in motion.
28. Why do frozen clothes lose water on a windy day?

# CHAPTER IX

## FUNDAMENTAL CHEMICAL LAWS

**101. The Balance.**—The chemical balance is the basis of modern research; and by its use during the past century the important laws of chemical combination were discovered. Lavoisier, during the latter part of the 18th century, recognized and laid stress upon the use of the balance as a trustworthy guide in chemical work. In so doing he laid the foundation for present research.

The balance consists of a beam delicately poised on an agate knife-edge so that it may swing with a minimum of friction. From the ends of the beam are suspended pans. In one pan is placed the object to be weighed; in the other pan is placed a number of weights to counterbalance. The standard weight is the **gram**, which is the thousandth part of a standard weight of metal known as a kilogram. The international kilogram prototype, an alloy of platinum-iridium, is kept at the International Bureau of Weights and Measures, near Paris.

**102. The Law of Conservation of Mass.**—In 1774 Lavoisier heated tin with air in a closed vessel, and observed that there was no change in the weight of the system notwithstanding the fact that the tin combined with oxygen of the air to form a white powder (stannic oxide). The conclusion arrived at by Lavoisier was stated thus:

> "Nothing can be created, and in every process there is just as much substance (quantity of matter) present before and after the process has taken place. There is only a change or modification of the matter."

It is quite generally supposed that the law of the conservation of matter was first formulated by Lavoisier, but the law was definitely enunciated by the Russian chemist Lomonossov, in 1756. Like Lavoisier, he heated tin in a closed vessel and found that there was no change in the weight of the system.

### DEMONSTRATION 37. LAW OF CONSERVATION OF MASS

**Materials:** Two-liter Erlenmeyer flask with rubber stopper, solutions of lead nitrate and potassium chromate, test-tube, large balance with weights and lead shot.

The test-tube containing potassium chromate rests in the large stoppered flask containing lead nitrate; and the whole is counterpoised on the balance. Upon tilting, the liquids mix; the lead nitrate and potassium chromate interact to form soluble, colorless potassium nitrate and insoluble, yellow lead chromate. When the flask is returned to the balance it will be seen that the weight has not changed during the reaction.

✓ **The Law of the Conservation of Mass**, or the Law of the Indestructibility of Matter, may be stated as follows: **The mass of a system is unaltered by any chemical change that occurs within it; or, when a chemical process is carried out, the total mass of the reactants is equal to the total mass of the products of reaction.**

DEMONSTRATION 38. LAW OF CONSERVATION OF MASS

Materials: Set-up illustrated in Fig. 53. The lime and caustic soda will absorb carbon dioxide and water.

When a candle burns, matter disappears and is seemingly destroyed. However, if the candle is counterpoised on a balance and the products of combustion caught, it will be found that these products weigh more than the original candle. This is because oxygen has been taken up from the air and increases the total weight of the products. Nothing has been destroyed; mass has been conserved throughout.

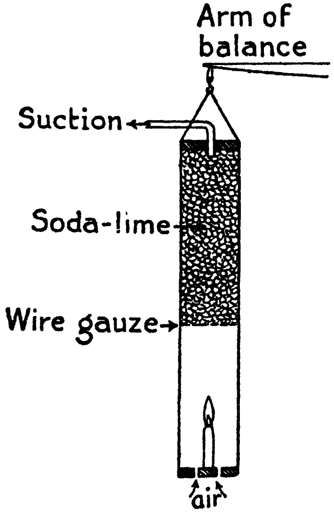
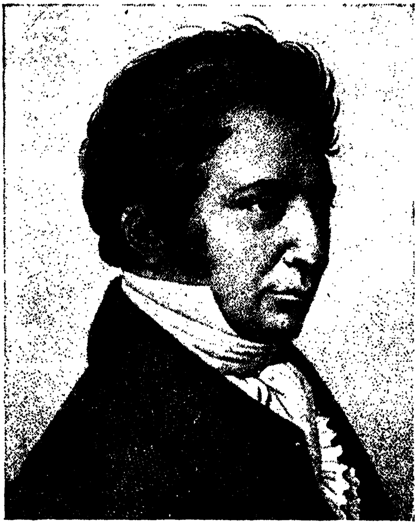


FIG. 53. Apparent increase in weight during combustion (Dem. 38).

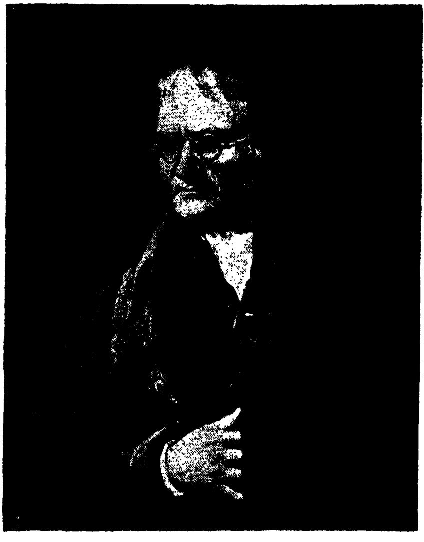
Many very careful experiments have been carried out to test the validity of the law. In 1893 Landolt began a series of experiments which were not completed until 1908. After a close examination of fifteen different reactions, he failed to observe a variation in weight greater than that within the limits of experimental error.

This law of the conservation of mass is one of the most fundamental laws of chemistry, inasmuch as the balancing of every chemical equation presupposes the validity of the law.



JOSEPH LOUIS GAY-LUSSAC (1778–1850)

Born at St. Leonard, he was educated at the École Polytechnique, where he became professor of chemistry, and at the same time professor of physics at the Sorbonne. In 1832 he accepted the chair of General Chemistry at the *Jardin des Plantes;* discovered (1808) his *law of combining volumes*, and independently the law of Charles; renowned for his work on iodine and cyanogen and their compounds.



JOHN DALTON (1766–1844)

Dalton was the eldest son of a poor weaver of Cumberland, England. Forced at an early age to rely upon his own efforts, he became a schoolmaster; well versed in mathematics and physics; an industrious investigator; discovered color-blindness (*Daltonism*); studied meteorology; formulated the *law of multiple proportions* and propounded the Atomic Theory.

**103. The Law of Definite Proportions.**—We have seen that the composition of water by weight is always the same (61). Whether pure water is synthesized or decomposed it is found to contain 11.19 per cent of hydrogen and 88.81 per cent of oxygen. This constancy of proportion extends to all compounds. As a result of thousands of experiments, chemists have reached the conclusion that **a particular compound always contains the same elements chemically united in the same proportions by weight.** This is known as the Law of Definite or Constant Proportions, or the law of constant composition.

Even before the nineteenth century chemists had shown that substances combined in definite proportions. Wenzel (1740–1793) showed that an hydroxide reacted with a definite weight of an acid to form water and a salt. J. B. Richter (1762–1817) carried out researches which further substantiated the doctrine of combining proportions by weight.

At the beginning of the nineteenth century, C. L. Berthollet and J. L. Proust carried on a celebrated controversy concerning the composition of compounds. Berthollet held that, in general, the composition of the product would vary with that of the original mixture. Proust held that the composition of a chemical compound is perfectly definite, and he conducted very careful experiments from 1799–1807. Proust was right, and is therefore regarded as the discoverer of the law of constant or definite proportions.

DEMONSTRATION 39. LAW OF DEFINITE PROPORTIONS

Materials: Set-up in Fig. 54.

The law may be illustrated experimentally by determining the percentage composition of copper oxide. A known weight of copper is heated in a stream of oxygen until the metal is transformed completely into copper oxide. The copper oxide is

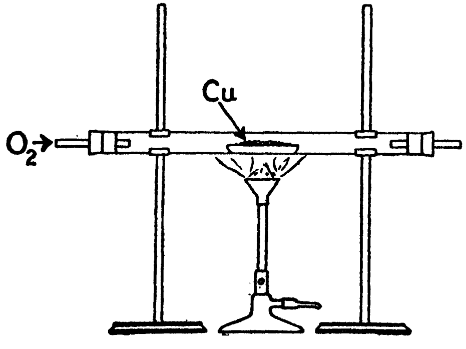


FIG. 54. Law of definite proportions (Dem. 39).

weighed. The gain in weight represents the weight of the oxygen. Knowing the weights of the copper and oxygen which unite, the percentage of each element in copper oxide can be shown.

The most accurate experiments show that pure copper oxide always contains 79.9 per cent of copper and 20.1 per cent of oxygen. In other words, it has a constant composition by weight. This is also true of all other chemical compounds.

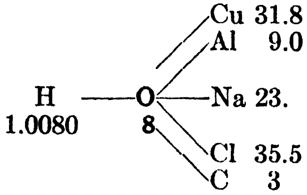
In terms of atoms and molecules the law of definite proportions follows naturally, for if a molecule is made up of a definite number of atoms, and the weights of those atoms never vary, then the ratios of those weights will also never vary. Thus if copper oxide is made up of one atom of copper, weight 63.6, and one atom of oxygen, weight 16, then the resulting molecule of copper oxide must weigh 79.6; and the percentage of copper in the compound will always be $\frac{63.6}{79.6}$, and the percentage of oxygen in the compound will always be $\frac{16}{79.6}$.

**104. The Law of Multiple Proportions.**—We have learned (20) that an element with variable valence may combine to form more than one compound with some other elements. Thus carbon combines with oxygen to form carbon monoxide, $CO$, and carbon dioxide, $CO_2$. Considering the weights of carbon and oxygen in these compounds it is evident that for every 12 grams of carbon, either 16 grams or 32 grams of oxygen will be present in these two oxides (atomic weights C 12, O 16). In the same way we may examine the relative weights of hydrogen and oxygen which combine to form the two compounds water (**61**) and hydrogen peroxide (**32, a(2)**). In this instance with the formulas $H_2O$ and $H_2O_2$, and the atomic weights H 1.008 and O 16, the combining weights would be $(2.016 + 16)$ in the case of water, and $(2.016 + 32)$ in the case of hydrogen peroxide. It is seen that the weight of oxygen in the latter case is exactly double that of the former case.

At the beginning of the nineteenth century this relationship was formulated as the **Law of Multiple Proportions** by John Dalton. It may be stated as follows:

**When two elements, A and B, unite to form more than one compound, the weights of B which unite with a fixed weight of A, stand to each other in the ratio of whole numbers, which are usually small.**

**105. The Law of Equivalent Weights.**—With the introduction of the chemical balance at the time of the American Revolution, considerable interest was focused on the weights of elements entering into chemical reactions. The German chemist, J. B. Richter, reported his researches from 1792–1799 on the "art of measuring chemical elements." Dalton, Berzelius, Stas and others extended the work of Richter. According to Sir Henry Roscoe, Cavendish (1731–1810) introduced the term **equivalent weight** to represent the relative weights of elements which combine with one another. As a result of all of these careful experiments the early chemist compiled a table of equivalent weights such as is illustrated below.



In the above table we see the weights of different elements combining with 8 parts of oxygen. **These combining weights of the elements referred to the scale of oxygen = 8, or hydrogen = 1.0080, are known as the equivalent weights.** Experimentally these equivalent weights are determined from data such as was obtained in demonstration 39. There it was shown that copper oxide contains 79.9 per cent of copper and 20.1 per cent of oxygen. From this the equivalent weight of copper, *i.e.*, the weight of copper combining with 8 grams of oxygen, is $x$ in the equation

$$\frac{79.9}{20.1} = \frac{x}{8},$$

$$x = \frac{79.9}{20.1} \times 8 = 31.80, \text{ the equivalent weight of copper.} \quad \text{ANS.}$$

It was found that these weights not only express the weights of elements combining with oxygen, but also the weights of these elements combining with one another. Thus from the table above we can read that 23 parts of sodium will combine with 35.5 parts of chlorine to form the compound sodium chloride, $NaCl$; and that 1.0080 parts of hydrogen will combine with 35.5 parts of chlorine to form hydrochloric acid, $HCl$. This fact can be utilized in the experimental determination of the equivalent weights of those elements which do not combine with oxygen. For in this case it is merely necessary to determine the weight of the element combining with a previously determined equivalent weight of some other element. Thus from the combining weights of hydrogen and oxygen the value 1.0080 can be experimentally determined for hydrogen. Using this figure, and determining the combining weights in the compound HCl, the value 35.5 may be arrived at for chlorine. Finally 23 g. of Na is found to combine with 35.5 g. of Cl in NaCl. The equivalent weight of Na is therefore 23.

In the case where an element may have variable valence, the weights of it combining with 8 parts of oxygen will be its equivalent weight or some multiple of it. **The Law of Equivalent Weights** may now be stated: **Elements combine with one another only in the proportions of their combining (equivalent) weights or of small multiples of them.**

**106. The Law of Combining Volumes of Gases.**—The reader is referred to Section 62 for a discussion of Gay-Lussac's law of combining volumes of gases. This law states that **when gases combine chemically, they do so in volumes which bear a simple ratio to one another, and to the volumes of the product if gaseous.** It was shown there that this remarkable relationship followed naturally from the law of Avogadro, namely, that at any given pressure and temperature equal volumes of different gases contain the same number of molecules. The words molecule and volume may therefore be used interchangeably in the equation which follows:

$$\begin{array}{ccccc} N_2 & + & 3H_2 & \rightarrow & 2NH_3. \\ \text{1 molecule} & + & \text{3 molecules} & \rightarrow & \text{2 molecules} \\ \text{1 volume} & + & \text{3 volumes} & \rightarrow & \text{2 volumes} \end{array}$$

**Reading References:** Articles number 65, 210 and 413 in the Appendix.

## QUESTION REVIEW

**The balance** (101).

1. Describe the chemical balance. What is the standard weight and to what is it referred? When did the balance come into general use?

I. THE LAW OF CONSERVATION OF MASS (102).

2. Who first definitely enunciated the law of conservation of mass?
3. Describe an experiment which proves that when a candle burns, matter is not destroyed.
4. Describe demonstration 37. Show why the law of conservation of mass is tacitly assumed in writing the equation for the reaction in this demonstration.

II. THE LAW OF DEFINITE PROPORTIONS (103).

5. Describe the experiment to determine the percentage composition of copper oxide.
6. Explain the law of definite proportions in terms of the atomic theory.

III. THE LAW OF MULTIPLE PROPORTIONS (104).

7. State the law of multiple proportions and explain it in terms of the atomic theory.

IV. THE LAW OF EQUIVALENT WEIGHTS (105).

8. Define equivalent weight. Show how the equivalent weight of copper may be determined experimentally.
9. Show how the equivalent weight of sodium can be determined indirectly rather than by measuring the parts of sodium combining with 8 parts of oxygen.
10. From the table in this section calculate the formula of the compound which carbon forms with chlorine (atomic weights Cl 35.5, C 12).

V. THE LAW OF COMBINING VOLUMES OF GASES (106).

11. Show that Avogadro's law explains the law of combining volumes of gases.
12. What volume changes are involved in the following reactions?

$$
\begin{aligned}
N_2 + 3H_2 &\rightarrow 2NH_3,\\
H_2 + Cl_2 &\rightarrow 2HCl,\\
2H_2 + O_2 &\rightarrow 2H_2O,\\
2Fe_{\text{solid}} + O_2 &\rightarrow 2FeO_{\text{solid}}.
\end{aligned}
$$

## CHAPTER X

## CHEMICAL ARITHMETIC

**107. Calculation of Percentage Composition from a Given Formula.**—The following plan is to be employed.

(*a*) The molecular weight (formula-weight) is found by summing up the atomic weights of the constituent elements.

(*b*) Since the molecular weight represents 100 per cent, the percentage of each element may be found thus:

$$\frac{\text{Mol. Wt.}}{\text{Wt. El.}} = \frac{100}{\%\ \text{El.}}.$$

$$\therefore \%\ \text{El.} = \frac{\text{Wt. El.}}{\text{Mol. Wt.}} \times 100.$$

(*c*) The sum of the percentages = 100.

*Problem.*—Calculate the percentage composition of potassium chlorate, $KClO_3$ [atomic weights K 39, Cl 35.5, O 16].

The formula-weight (molecular weight) of potassium chlorate is the sum of the atomic weights, which is

$$39 + 35.5 + 16 \times 3 = 122.5.$$

This means that in 122.5 g. (1 gram-molecule) of potassium chlorate there are 39 g. of potassium, 35.5 g. of chlorine, and 48 g. of oxygen.

The *percentage of potassium* can be calculated as follows:

$$\frac{122.5}{39} = \frac{100}{x};\ \text{or,}$$

$$x = \frac{39}{122.5} \times 100 = 31.84 \text{ per cent.}$$

$$\textit{Percentage of chlorine} = \frac{35.5}{122.5} \times 100 = 28.98.$$

$$\textit{Percentage of oxygen} = \frac{48}{122.5} \times 100 = 39.18.$$

The sum of the percentages is, of course, 100:

$$31.84 + 28.98 + 39.18 = 100.$$

This is, therefore, a check on the accuracy of the work.

**108. Derivation of Chemical Formula from Percentage Composition.**—The following plan is to be adopted.

(*a*) Divide the per cent of each element in the compound, or the weights of the elements which unite, by their atomic weights. This gives the ratio of atoms in the molecule.

(*b*) Divide all of the quotients in (*a*) by the smallest quotient. This gives the relative number of atoms in a molecule of the compound. From this the simplest formula of the compound is apparent.

*Problem.*—1.246 g. of copper combines with 0.310 g. of oxygen to form cupric oxide. Atomic weights Cu 63.57, O 16. What is the formula of copper oxide?

| | Weights of the elements | Gram-atomic weights of the elements | Ratio of atoms in the molecule | Number of atoms |
|---|---|---|---|---|
| Copper | 1.246 g. | 63.57 | 1.246/63.57 = 0.0196 | 1 |
| Oxygen | 0.310 g. | 16 | 0.310/16 = 0.0194 | 1 |

Simplest formula is therefore $CuO$. ANS.

*Problem.*—A compound was analyzed and found to contain 43.39% sodium, 11.32% carbon, and 45.29% oxygen. Atomic weights are Na 23, C 12, O 16. What is the simplest formula of the compound?

| Element | % | Atomic weights | Ratio of atoms in the molecule | Number of atoms |
|---|---|---|---|---|
| Sodium | 43.39 | 23 | 43.39/23 = 1.88 | 2 |
| Carbon | 11.32 | 12 | 11.32/12 = 0.94 | 1 |
| Oxygen | 45.29 | 16 | 45.29/16 = 2.82 | 3 |

Simplest formula is therefore $Na_2CO_3$. ANS.

Occasionally the number of atoms in the last column may have to be further operated upon to give simple whole numbers. This is exemplified in the next problem.

*Problem.*—Derive the simplest formula for aluminum oxide, which contains 52.94% of aluminum and 47.06% of oxygen.

| % of the elements | | Atomic weights | Ratio of atoms in the molecule | Number of atoms |
|---|---|---|---|---|
| Aluminum | 52.94 | 27 | 1.96 | 1 |
| Oxygen | 47.06 | 16 | 2.94 | 1.5 |

Since fractions of molecules do not take part in chemical changes, we cannot represent the formula unless we multiply the numbers in the last column by 2. In this case

Simplest formula is $Al_2O_3$. ANS.

## CALCULATIONS USING EQUATIONS

**109. Weight-Weight Problems.**—We normally think of the formula of a molecule, such as $CaCO_3$, representing 1 molecule of substance. In the use of equations for calculations, however, this formula represents a **mole** of substance. **1 mole of substance is its molecular weight in grams.** $CaCO_3$ (calcite) can therefore stand for 1 gram-molecular weight of calcite, which is the sum of the atomic weights of its constituent elements, viz. 40 + 12 + (3 × 16) g. = 100 g. The equation therefore represents a reaction between a definite quantity of material. For example in the treatment of calcite with acid we have

$$\begin{gathered} CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2, \\ 1 \text{ mole} + 2 \text{ moles} \rightarrow 1 \text{ mole} + 1 \text{ mole} + 1 \text{ mole}, \\ 100 \text{ g.} + 2 \times 36.5 \text{ g.} \rightarrow 111 \text{ g.} + 18 \text{ g.} + 44 \text{ g.} \end{gathered}$$

These relations of the weights of reacting substances and of the products formed enable us to utilize chemical equations in calculations.

*Problem.*—What weight of oxygen is required to burn 4 g. of pure carbon (atomic weights C 12, O 16)?

The steps for solving this problem follow.

| | | | | | | |
|---|---|---|---|---|---|---|
| Step 1 | Balance equation | C | + | $O_2$ | → | $CO_2$ |
| Step 2 | Problem, $x$ unknown | 4 g. | + | $x$ g. | | |
| Step 3 | Weight-Weight relations | 12 g. | + | 32 g. | | |
| Step 4 | Proportion | $\frac{4}{12}$ | = | $\frac{x}{32}$ | | |

$$x = \frac{4 \times 32}{12} = 10.7 \text{ g. } O_2. \quad \text{ANS.}$$

*The proportion should not be blindly applied.* The student should read this "4 grams of carbon require how many grams of oxygen, if 12 grams of carbon require 32 grams of oxygen?"

An alternative method of solving this is by the use of moles, as follows.

| | | | | | | |
|---|---|---|---|---|---|---|
| Step 1 | Balance equation | C | + | $O_2$ | → | $CO_2$ |
| Step 2 | Problem, $x$ unknown | 4 g. | | $x$ g. | | |
| Step 3 | Moles and gram-molecular weights | 1 mole<br>12 g. | | 1 mole<br>32 g. | | |
| Step 4 | Calculation | | | | | |

4 grams of carbon represent 4/12 moles of carbon. According to the equation this would require 4/12 moles of oxygen. Since 1 mole of oxygen weighs 32 grams, the oxygen required would be $x = 4/12 \times 32 = 10.7$ g. $O_2$. ANS.

**110. Volume-Volume Problems.**—In the same way, **1 mole of gaseous substance represents 22.4 liters at S.T.P.**, and this may be applied in solving problems involving volumes of reacting gases or their products.

*Problem.*—What volume of hydrogen chloride gas is obtained by burning 4 liters of hydrogen in chlorine?

| | | | |
|---|---|---|---|
| Step 1. . . . Balance equation . . . . . . . | $H_2$ | $+ Cl_2 \rightarrow$ | $2HCl$ |
| Step 2. . . . Problem, $y$ unknown. . . . . | 4 l. | | $y$ l. |
| Step 3. . . . Volume-Volume relations. | 22.4 l. | | 44.8 l. |
| Step 4. . . . Proportion. . . . . . . . . . . . . | 4/22.4 | | $= y/44.8$ |

$$y = \frac{4 \times 44.8}{22.4} = 8 \text{ l. HCl.} \quad \text{ANS.}$$

The proportion is read "4 liters of hydrogen will form what volume of hydrogen chloride, if 22.4 liters of hydrogen form 44.8 liters of hydrogen chloride?"

The same problem expressed as a mole problem would be solved as follows.

| | | | |
|---|---|---|---|
| Step 1. . . . Balance equation | $H_2$ | $+ Cl_2 \rightarrow$ | $2HCl$ |
| Step 2. . . . Problem, $y$ unknown | 4 l. | | $y$ l. |
| Step 3. . . . Moles and gram-molecular volumes | 1 mole<br>22.4 l. | | 2 moles<br>44.8 l. |
| Step 4. . . . Calculation | | | |

If 1 mole of hydrogen will give 2 moles of hydrogen chloride, 4/22.4 moles of hydrogen will give 2 × 4/22.4 = 8 liters of hydrogen chloride. ANS.

The calculations must be made at the same temperature and pressure.

**111. Weight-Volume Problems.**—A combination of the methods presented in the preceding two sections is used in solving a third type of problem, illustrated below.

*Problem.*—What volume of oxygen at S.T.P., will be obtained by heating 6 g. of potassium chlorate, $KClO_3$ (atomic weights K 39, Cl 35.5, O 16)?

| | | | |
|---|---|---|---|
| Step 1. . Balance equation. . . . . . . | $2KClO_3 \rightarrow$ | $2KCl +$ | $3O_2$ |
| Step 2. . Problem, $z$ unknown. . . . | 6 g. | | $z$ l. |
| Step 3. . Weight-Volume relations | 2(39 + 35.5 + 48) g. | | 3(22.4) l. |
| Step 4. . Proportions. . . . . . . . . . . . | 6/245 g. | | $z$/67.2 l. |

$$z = \frac{6 \times 67.2}{245} = 1.64 \text{ l. } O_2. \quad \text{ANS.}$$

The same problem solved by the use of moles is

| | | | |
|---|---|---|---|
| Step 1. . . . Balance equation | $2KClO_3 \rightarrow$ | $2KCl +$ | $3O_2$ |
| Step 2. . . . Problem, $z$ unknown | 6 g. | | $z$ l. |
| Step 3. . . . Moles | 2 moles<br>2(39 + 35.5 + 48) g. | | 3 moles<br>3(22.4) l. |
| Step 4. . . . Calculations | | | |

If 1 mole of $KClO_3$ gives 3/2 moles of oxygen, or 22.4 × 3/2 liters of oxygen, then 6/245 moles of $KClO_3$ will give

$$(6/245) \times (22.4 \times 3/2) \text{ liters} = 1.64 \text{ liters } O_2. \quad \text{ANS.}$$

## QUESTION REVIEW

*Note: In the following problems make use of the atomic weights in the table on the inside front cover of the text.*

### I. Formulas and percentage composition.

**a. Percentage composition from a given formula (107).**

1. Calculate the percentage composition of (*a*) HgO; (*b*) $CuSO_4, 5H_2O$; (*c*) $NaNO_3$.

**b. Formula from percentage composition (108).**

2. 1.972 g. of metallic gold was obtained upon decomposing 2.212 g. of an oxide of gold by heat. Find the simplest formula of the compound.
3. A compound contains 32.43% sodium, 22.55% sulfur, and 45.02% oxygen. Find its simplest formula.

### II. Calculations using equations.

**a. Weight-weight problems (109).**

4. What weight of oxygen is required to burn 8 g. of sulfur? What weight of sulfur dioxide is formed?
5. What weight of carbon dioxide could be produced by strongly heating 15 g. of pure marble ($CaCO_3$)? $CaCO_3$ (heated) $\rightarrow CaO + CO_2$.
6. What weight of carbon dioxide is obtained by treating 100 g. of calcium carbonate with an excess of hydrochloric acid?
7. If 2.55 g. of silver nitrate is dissolved in water and then treated with excess sodium chloride, what will be the weight of the precipitate?

**b. Volume-volume problems (110).**

8. What volume of hydrogen chloride gas at S.T.P. would be formed by burning 253 cc. of hydrogen in chlorine?
9. What weight and what volume at 760 mm. pressure and 327° C. of sulfur dioxide will be obtained by burning 20 grams of sulfur?

**c. Weight-volume problems (111).**

10. What volume of hydrogen at S.T.P. is obtained by treating 6.54 g. of zinc with an excess of sulfuric acid? If this is exploded with oxygen, what volume of steam at 100° C. will be formed?
11. A specimen of potassium chlorate was strongly heated and the volume of gas evolved was found to be 520 cc.

when measured over water at 20° C. and under a pressure of 772.4 mm. Find the volume of the *dry* gas at S.T.P. [*Aqueous tension* at 20° C. = 17.4 mm.]

12. 20 g. of zinc was treated with 73 g. of dilute hydrochloric acid containing 10% HCl by weight. The gas evolved was collected over water, in a room where the barometric pressure was 750.4 mm. and the temperature 68° F. What was the observed volume?
13. What weight of potassium chlorate must be heated to prepare 100 cc. of gas, assuming that it is measured over water at 17° C. and 764 mm.? [*Aqueous tension* at 17° C. = 14 mm.]
14. What weight and what volume of hydrogen would be liberated by dissolving 2.5 gram-atoms of zinc in dilute sulfuric acid? What weight of zinc sulfate would be formed?

# CHAPTER XI

## DETERMINATION OF ATOMIC AND MOLECULAR WEIGHTS

**112. Importance of Weights.**—There are probably no atomic data more fundamental than the relative weights of atoms and molecules. Each shipment of ore, each carload of raw materials, each finished chemical product has from time to time during its manufacture been subjected to chemical analysis involving atomic weights. The iron metallurgist must analyze for impurities in his pig iron, or his steel will be imperfect. The industrialist who buys tons of silver ore must receive a report on its silver content. The druggist must carefully weigh his ingredients; and, if they are to react chemically, this involves a calculation using equivalent or combining weights. In fact in all of these cases chemical analyses must be carried out, equations must be written, and calculations must be made using the equations and the atomic weights which they represent. So important is it that there be a universal agreement as to atomic weights, that an International Committee on Atomic Weights each year submits an official table, based on new data accumulated during the preceding year. Newly devised experiments for removing impurities, and new and more accurate instruments, make it possible to improve some of the weights from year to year.

**113. The Mass Spectrograph. Isotopes.**—In the past, the determination of atomic weights has been by chemical methods. First, however, we shall describe an instrument which, although invented two decades ago, has become an apparatus of precision only since 1927, and is now an important factor in deciding atomic weights. It is called a **mass spectrograph**; for it separates particles into a line spectrum according to their weights, or masses, just as an ordinary spectrograph separates light into a spectrum of colors. In 1937 the mass spectrograph was instrumental in changing the atomic weight of carbon from 12.00 to 12.01; and of phosphorus from 31.027 to 30.978.

Chlorine has an atomic weight of 35.457. We should accordingly expect that an analysis of chlorine gas in the mass spectrograph would give a line at 35.457. Such is not the case. Instead *two* lines are obtained, one at 35 and the other at 37, the relative intensities of these lines being 75.4 and 24.6. That is, chlorine is a mixture of 75.4% of chlorine with atomic weight 35, and 24.6% of chlorine of atomic weight 37; and the composite weight of this mixture is roughly (75.4% × 35) + (24.6% × 37) = 35.457. These two kinds of chlorine atoms are called **isotopes of chlorine.** It is an amazing fact that the ratio of these two isotopes is always 75.4 : 24.6 for every known chlorine compound throughout the world. This points to a common origin of all of the chlorine in the world. **Most of the 92 elements have isotopes.**

All mass spectrographs produce positive ions, such as $Cl_2^+$, $O_2^+$, $O_2^{++}$, by shearing electrons from gaseous molecules; and then these positive ions are passed through electric and magnetic fields so arranged that particles of the same value for *m/e* (*i.e.*, mass/charge) are focused upon the same spot. The earliest machines were made by Sir J. J. Thompson (1911) and F. W. Aston (1913–40). Aston's lifework has been devoted to the study of isotopes, culminating (1927) in his developing a machine which could estimate the masses of particles with an accuracy of 1 part in 10,000.

Dempster (1918–22, 1935) and Bainbridge (1932, 1936) developed the precursors of a machine invented in 1940 by E. O. Nier. The machine is shown in Fig. 55. This particular machine is illustrated because its low cost and simplicity has led to its current popularity and wide-spread adoption in analyzing isotopes in many universities.

The Nier mass spectrograph is evacuated to one millionth of a millimeter of mercury pressure, and the gas to be analyzed is

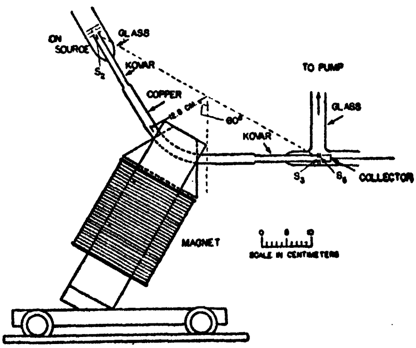


FIG. 55. Nier mass spectrograph.

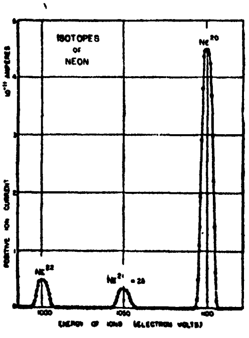


FIG. 56. Results with Nier instrument.

allowed to leak into the portion of the apparatus marked "ion source." This leak is so small that only 12 mm. of gas pressure is built up in the apparatus in 20 minutes. The gas is bombarded by low velocity electrons, which tear electrons from the gas and produce positive ions (*e.g.*, $(^{35}Cl)_2^+$, $(^{37}Cl)_2^+$). The positive ions are accelerated by a series of grids similar to those in a radio amplifying tube. The positive particles pass through slit $S_2$ into the tube of kovar, a special alloy for making a vacuum tight seal between glass and copper. Entering the adjacent copper tube, the positive ions pass between the poles of a powerful magnet, bending the ions through a 60° arc, and focusing particles of some fixed $m/e$ value upon slit $S_3$. From here they pass into collector $S_5$. Only those particles reach the collector which have the following relation of mass $m$, charge $e$, radius of copper tube $r$, magnetic field strength H, and velocity $v$:

$$m/e = 4.82 \times 10^{-5}\, r^2\, \mathrm{H}^2/v.$$

From this equation it appears that if the field strength H is altered, particles of different mass $m$ reach the collector. The collector leads to an amplifier which operates a galvanometer; and from the deflection of the latter the number of particles which reach the collector may be calculated.

A typical result for neon is shown in Fig. 56. Neon has the isotopes $^{20}$Ne 90.00%, $^{21}$Ne 0.27%, $^{22}$Ne 9.73%; and these percentages are indicated by the relative heights of the peaks corresponding to these weights.

Another type of mass spectrograph substitutes a photographic plate for the collector. The positive ions register as lines upon the plate, and their positions and darkness indicate the relative abundance of different isotopes. An examination of Fig. 57 reveals, for example, which isotopes of Cd are most abundant. Compare with Table 51, page 293.

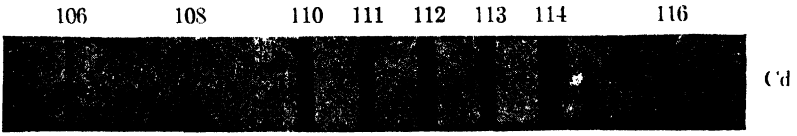


FIG. 57. Mass spectra of cadmium (Dempster).

A good example of the accurate determination of atomic weights by the use of the mass spectrograph is given for the element chromium. The abundance of chromium isotopes is $^{52}$Cr 81.6%,

$^{53}$Cr 10.4%, $^{50}$Cr 4.9%, $^{54}$Cr 3.1%. The atomic weight is roughly $(81.6\% \times 52) + (10.4\% \times 53) + (4.9\% \times 50) + (3.1\% \times 54) = 52.0680$, which, after certain necessary corrections,[1] gives an accurate value of 52.0046. This compares favorably with the accepted chemical value of 52.01, but suggests that a redetermination by the chemical method would not be out of place.

**114. Indirect Methods of Determining Weights.**—Unfortunately the method of the mass spectrograph is the only one which determines atomic and molecular weights simply and directly. In the other methods which will be described below it is necessary (*a*) to determine *approximate* weights and then (*b*) to use these in determining *exact* weights. An outline of these indirect methods can be seen in the question review at the end of this chapter.

### APPROXIMATE WEIGHTS

**115. Approximate Molecular Weight of a Gas (Weight of 22.4 Liters).**—In discussing the kinetic-molecular theory (96) the fact was stressed that equal volumes of different gases under the same conditions of temperature and pressure contained the same number of molecules (Avogadro's law). If we should compare the weight of some oxygen molecules with the weight of an equal number of carbon dioxide molecules, this will obviously be the ratio of the weights of these two molecules relative to each other. Similarly, the ratio of the weights of equal volumes of these two gases will give their relative molecular weights. Now the molecular weight of oxygen is 32, and it is found by experiment that 32 grams of oxygen fill 22.4 liters at S.T.P. If we weigh 22.4 liters of carbon dioxide we find it to be 44 grams. From the above reasoning the molecular weight of carbon dioxide is 44.

A general method for determining approximate molecular weights of any gas therefore consists in finding the weight of 22.4 liters of that gas at S.T.P. **22.4 liters is called the gram-molecular volume.** The gram-molecular volumes of four common gases are shown in Fig. 58. Experimentally the chemist weighs a known volume of the gas at some given temperature and pressure, and from these data calculates the weight of 22.4 liters of the gas at S.T.P.

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[1] From 52.068 must be subtracted 0.0114, a number which takes into account the fact that oxygen contains not only $^{16.0000}$O but $^{18}$O and $^{17}$O as well; and 0.0520, a number which corrects for a change in weight due to packing in the chromium nucleus. $52.0680 - 0.0114 - 0.0520 = 52.0046$.

*Example.*—111.4 cc. of a gas, measured dry and at 27° and 750 mm., weigh 0.1537 g. What is its molecular weight?

$$V_{(\text{S.T.P.})} = 111.4 \times \frac{273}{300} \times \frac{750}{760} = 100 \text{ cc.}$$

100 cc. weigh 0.1537 g., or 1 liter weighs 1.537 g.; therefore 22.4 liters weigh 22.4 × 1.537 = 34.43, the molecular weight. ANS.

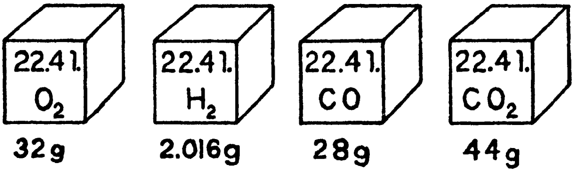


FIG. 58. The gram-molecular volume. One mole of any gas occupies 22.4 liters.

The student should clearly realize that the veracity of Avogadro's Law is implied in determining molecular weights by this method. However, because of attractive forces between different kinds of molecules, the law is not strictly accurate. For example, the exact gram-molecular volumes of a number of gases follow.

TABLE 20. DEVIATIONS FROM 22.4 LITERS PER MOLE AT S.T.P.

| Gas | Formula | Gram-Molecular Weight = 1 gram-mole | Volume occupied by 1 gram-mole |
|---|---|---|---|
| Ammonia | $NH_3$ | 17 g. | 22.084 liters |
| Carbon dioxide | $CO_2$ | 44 g. | 22.264 " |
| Hydrogen | $H_2$ | 2 g. | 22.423 " |
| Nitrogen | $N_2$ | 28 g. | 22.405 " |
| Oxygen | $O_2$ | 32 g. | 22.394 " |

From this it is seen that use of the value 22.4 liters gives only an approximate and *not an exact molecular weight.*

Application of this relation between gram-molecular weight and 22.4 liters may be employed in calculating the weight of a liter of any gas, given its molecular weight; for in this case

$$\text{wt. of 1 liter of a gas} = \frac{\text{gram-molecular weight}}{22.4}.$$

**116. Approximate Molecular Weight of a Liquid (Vapor Density of 22.4 Liters).**—The molecular weight of a liquid which may be readily vaporized may likewise be determined by use of the weight of 22.4 liters of its vapor.

**Dumas** (1826) volatilized a few grams of liquid by heating it in a light glass bulb provided with a long neck. When the bulb became filled with vapor, the neck was sealed and the weight of the vapor and the volume of the bulb determined.

**Victor Meyer** (1877) measured the volume of air displaced by the vapor from a known weight of the volatile substance.

The apparatus is shown in Fig. 59. It consists of an inner tube *B* surrounded by an outer tube or jacket *A*, in the bottom of which is placed a substance with a boiling point 30° or more higher than that of the liquid the vapor density of which is to be determined. A small closed bottle (or bulb) containing a known weight of the liquid is introduced into the inner tube by removing the stopper, being arrested by a movable shelf placed at *D*. The tube is tightly stoppered, the liquid in the bulb of the jacket boiled until the temperature of the inner tube is constant, the expanding air being allowed to escape through the side-tube into the atmosphere. When no more bubbles of gas escape from the end of the delivery tube, the graduated tube *F* containing water (or mercury) is clamped in position. The shelf *D* is now pulled aside and the little bottle containing the liquid falls to the bottom of the inner tube. The liquid vaporizes rapidly and blows the stopper out of the bottle, and the rising vapor displaces its own volume of air which collects in the tube *F*. This volume of air is now measured at atmospheric pressure, and the temperature and barometric pressure noted. From these data and the weight of the liquid undergoing vaporization the density of the vapor may be readily calculated, and from this value the molecular weight found.

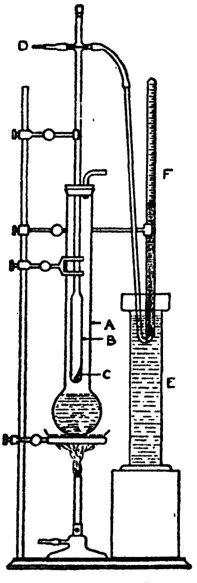


FIG. 59. Victor Meyer vapor density apparatus.

*Example.*—0.150 g. of chloroform was volatilized by means of boiling water, and the resulting vapor displaced 30.5 cc. of air, measured over water at 22° C., the barometric pressure being 755 mm. Find the vapor density of chloroform and then calculate its molecular weight.

*Note.*—First find the volume of dry air at S.T.P., which corresponds to the volume of 0.150 g. of chloroform vapor under the same conditions. Chemical analysis shows that the formula of chloroform is $(CHCl_3)_x$, in which $x$ is a whole number.

It is understood, of course, that the vapor density method cannot be employed for the determination of the molecular weights of substances which decompose on heating, *e.g.*, the sugars. Since these latter compounds are often soluble, their molecular weights may be determined by other methods, such as the following.

**117. Approximate Molecular Weight by Depression of Freezing Point.**—When certain substances such as alcohols and sugars

Amadeo Avogadro (1776–1856)

Professor of Physics at Turin. In 1811 he proposed the important hypothesis associated with his name. He was the first scientist to draw a distinction between molecules and atoms. Avogadro's law has been one of the most useful in chemistry, enabling chemists to determine the molecular weights of gases.

are dissolved in water the solution will freeze below 0° C. 1 gram-molecular weight of substance dissolved in 1,000 grams of water lowers the freezing point approximately 1.86°. 2 gram-molecular weights lower it twice as much, that is 3.72°. From this it is seen that the depression of the freezing point of water is directly proportional to the quantity of solid dissolved in it. This is illustrated in Table 21.

TABLE 21. DEPRESSION OF F.P.

| Name of Substance | Formula | Wt. of 1 Mole | Depression of F.P. |
|---|---|---|---|
| Methyl alcohol | $CH_4O$ | 32 g. | −1.86° C. |
| Ethyl alcohol | $C_2H_6O$ | 46 g. | " |
| Glucose | $C_6H_{12}O_6$ | 180 g. | " |
| Cane sugar | $C_{12}H_{22}O_{11}$ | 342 g. | " |
| " " | " | 684 g. = 2 moles | −3.72° C. |

The approximate molecular weight of such substances can therefore be determined by ascertaining the weight of the substance which is required in order to lower the freezing point of 1,000 grams of water to −1.86° C.

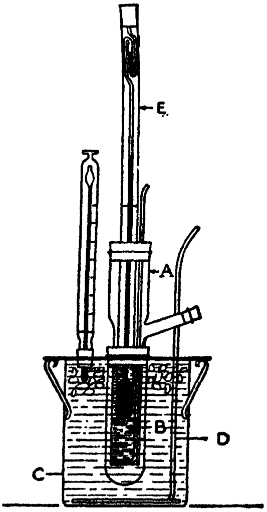


Fig. 60. Beckmann freezing point apparatus.

*Example.*—90 g. of glucose lowers the freezing point of 250 g. of water to −3.72° C. What is the approximate molecular weight of glucose?

90 g. in 250 cc. is 90 × 1000/250 = 360 g. per 1000 g. water. Since the F.P. was lowered −3.72°, there must have been −3.72/−1.86 = 2 moles of glucose per 1000 g. of water. If 360 g. is 2 moles, the molecular weight of glucose is 360/2 or 180. ANS.

The **Beckmann Apparatus** is used in determining approximate molecular weights by the freezing point, or cryoscopic, method.

It consists of a tube *A* with a side-tube, which is sunk into a wider tube in order to surround the former by an air space (Fig. 60). A heavy glass jar *C* contains a freezing mixture which is stirred by the stirrer *D*. The inner tube is fitted with a Beckmann thermometer and a stirrer. A known weight of the solvent is placed in tube *A*, its freezing point determined, and then a weighed quantity of the solute is introduced through the side-tube, and the freezing point of the solution (*B*) determined. The difference between this number and the freezing point of the pure solvent gives the depression of the freezing point.

As will be treated in Sections 183–184, solids dissolved in water also alter other of its physical properties; and these too may be used in determining approximate molecular weights.

The method cannot be used for acids, hydroxides, and salts (182).

**118. Approximate Atomic Weight from Molecular Weight × % of Element in Compounds.**—There are two steps in this method. First the molecular weights of 22.4 liters at S.T.P. of a number of volatile compounds containing the elements are determined. Second, the compounds are analyzed to determine the percentage of the element in each of these compounds.

The calculations using these data may be illustrated in the case of carbon monoxide, CO. The gram-molecular weight of CO is 28. The percentage of carbon in this molecule is 42.9. The weight of carbon in this molecule is therefore 28 × 42.9 = 12.0. The weight of an atom of carbon would therefore appear to be 12.0. If a similar determination is carried out for acetylene, $C_2H_2$, the weight of the carbon in the molecule, as given by the weight of 22.4 liters × the percentage of carbon in the molecule, is approximately 24. This is because there are two atoms of carbon in the molecule, each weighing 12. This method therefore gives either the atomic weight of carbon or a multiple of it, depending upon how many atoms of carbon there are in the compound being tested. In practice, data are collected for a number of volatile compounds containing the element in question and the smallest value obtained is taken as the atomic weight. This is illustrated in Table 22. Since this method is based upon the use of 22.4 liters, it gives only approximate weights.

TABLE 22. THE DETERMINATION OF ATOMIC WEIGHTS

| Compound | Formula | M, or the Wt. of 22.4 Liters | Per Cent of El. | Wt. of El in M = M × per cent El. |
|---|---|---|---|---|
| Carbon monoxide | $CO$ | 28.0 | 42.9 | 12.0 |
| Carbon dioxide | $CO_2$ | 44.3 | 27.3 | 12.1 |
| Methane | $CH_4$ | 16.0 | 74.9 | 12.0 |
| Acetylene | $C_2H_2$ | 26.1 | 92.3 | 24.1 |
| Benzene | $C_6H_6$ | 77.7 | 92.3 | 71.7 |
| Chloroform | $CHCl_3$ | 118.7 | 10.4 | 12.3 |
| Alcohol | $C_2H_6O$ | 45.6 | 52.2 | 23.8 |

The method just developed applies only to elements such as carbon, chlorine, and nitrogen that form a considerable number of stable gaseous or volatile compounds. If a compound should ever be discovered containing 6 g. of carbon in the mole, *i.e.*, in 22.4 liters of the gas at S.T.P., the atomic weight of carbon would be reduced to one-half of its present value; but we are sure now that such a discovery will never be made.

**119. Approximate Atomic Weight of a Solid from Specific Heat.**—In 1818 Dulong and Petit, of Paris, enunciated the **Law of Specific Heats**, which may be stated thus: **The atomic heat of a solid element is approximately constant, and equals 6.4.** The atomic heat is the product of the atomic weight × the specific heat. An examination of specific heat data in Table 23 shows the value 6.4 is only approximate, so that this method of determining atomic weights gives approximate values only.

TABLE 23. SPECIFIC AND ATOMIC HEATS OF SOME SOLID ELEMENTS

| Element | Atomic Weight | Specific Heat | Atomic Heat |
|---|---|---|---|
| Lithium | 6.94 | 0.9063 | 6.29 |
| Sodium | 23.00 | 0.2829 | 6.51 |
| Silver | 107.88 | 0.0590 | 6.36 |
| Lead | 207.22 | 0.0310 | 6.42 |
| Uranium | 238.14 | 0.0280 | 6.67 |

### DEMONSTRATION 40. DETERMINATION OF SPECIFIC HEAT

Materials: 400 cc. beaker jacketed with cotton, and set in an 800 cc. beaker. Thermometer passing through asbestos cover to the bottom of the smaller beaker. A second thermometer immersed in 200 g. lead shot in a 30 × 250 mm. test tube, nearly submerged in boiling water. A beaker containing exactly 200 cc. of water.

While the lead is coming to constant temperature, pour the 200 cc. of cold water into the 400 cc. beaker, and record its temperature. Record the temperature of the lead shot. Quickly pour the shot into the beaker of cold water, stir vigorously with the thermometer, and record the temperature as soon as equilibrium is reached. From these data the specific heat of lead is calculated, for

$$\text{sp. ht.} = \frac{\text{weight of water} \times \text{rise in temperature of water}}{\text{weight of lead} \times \text{drop in temperature of lead}}.$$

## EXACT WEIGHTS

**120. Exact Atomic Weight from Equivalent Weights.**—It will be recalled that the equivalent weight is an experimental value which represents the weight of the element combining with 8 grams of oxygen or 1.0081 grams of hydrogen. Approximate atomic weights may be determined by the methods described in Sections 118 and 119.

The exact atomic weight is calculated by multiplying the equivalent weight, which is an exact weight, by that simple whole number which brings it closest to the approximate atomic weight.

*Example 1.*—The equivalent weight of cadmium is found to be 56.2. The specific heat of cadmium is 0.0568. Find the exact atomic weight of cadmium.

$$\text{Approximate atomic weight} = \frac{6.4}{0.0568} = 114.3.$$

Since this value is approximately twice the exact equivalent weight, we have

Exact atomic weight = 56.2 × 2 = 112.4. ANS.

*Example 2.*—24.02 g. of carbon combines with 64 g. of oxygen. The approximate atomic weight of carbon (see Table 22) is 12. What is the exact atomic weight of carbon?

Equivalent weight of carbon = weight of carbon combining with 8.0 g. of oxygen = 24.02 × 8/64 = 3.0025.

Exact atomic weight = 3.0025 × 4 = 12.010. ANS.

The whole number by which the equivalent weight must be multiplied to raise it to a value nearly equal to the approximate atomic weight is really the valence of the element. That is,

**Atomic weight = Equivalent weight × Valence.**

**121. Exact Molecular Weight.**—Chemical analysis can establish percentage composition and, from that, molecular formulas (**108**). The exact molecular weight will then be the sum of all the exact atomic weights (**120**) of its constituent atoms.

*Example.*—What is the exact molecular weight of magnesium chloride? Since the exact atomic weights of magnesium and of chlorine are 24.32 and 35.457 respectively, the

Exact molecular weight of $MgCl_2$ = 24.32 + (2 × 35.457) = 95.23. ANS.

Occasionally the simplest formula is not the complete formula. For instance, CH is the simplest formula for both acetylene, $C_2H_2$, and for benzene, $C_6H_6$. In such a case the simplest formula is established (**108**) and compared with the approximate molecular weight (**115–117**). The sum of the exact atomic weights (**120**) is then multiplied by that whole number bringing it closest to the approximate molecular weight. This product is the exact molecular weight.

*Example.*—A gas is found to contain 92.3% carbon, and 7.7% hydrogen. 22.4 liters of the gas weighs 78 g. What is the exact molecular weight of the gas? (C = 12.010, H 1.0081)

Step 1....C....92.3/12 = 7.7....1
H.... 7.7/ 1 = 7.7....1....Simplest formula = CH
Step 2....Since 22.4 liters of the gas weighs 78 g., the approximate molecular weight of the gas is 78.
Step 3....CH is 12.010 + 1.0081 = 13.018
Exact molecular weight = 6 × 13.018 = 78.108. ANS.

**122. Derivation of Molecular Formulas of Elements.**—We have already learned that many gases are diatomic, *e.g.*, chlorine, $Cl_2$. The evidence for this is that the weight of 22.4 liters of chlorine at S.T.P. is twice as great as the atomic weight of chlorine. There must therefore be 2 atoms of chlorine in each molecule. Similar data for a number of other elements are given in the following Table.

TABLE 24. MOLECULAR FORMULAS FOR ELEMENTS

| Element | Symbol | Atomic Weight | Molar Weight, *i.e.*, the Weight of 22.4 Liters | Formula of Free Element |
|---|---|---|---|---|
| Oxygen | O | 16.00 | 32 | $O_2$ |
| Ozone | O | 16.00 | 48 | $O_3$ |
| Hydrogen | H | 1.008 | 2.016 | $H_2$ |
| Nitrogen | N | 14.008 | 28.016 | $N_2$ |
| Phosphorus | P | 30.978 | 124.12 | $P_4$ |
| Sodium | Na | 23.00 | 23 | Na |
| Zinc | Zn | 65.38 | 65.38 | Zn |
| Mercury | Hg | 200.61 | 200.61 | Hg |

**123. Derivation of Molecular Formulas of Compounds.**—Both acetylene, $C_2H_2$, and benzene, $C_6H_6$, have the simplest formula, CH. This simplest formula may be derived experimentally by the method described in Section 108. To derive the exact formulas in the two cases, however, an additional step must be taken. The approximate molecular weights of the two substances must be determined. When this is done (115–117) it is found that the approximate molecular weights of acetylene and of benzene are 25 and 78 respectively. The weight of the simplest formula, CH, is 12 + 1 or 13. Acetylene therefore has 25/13 or 2CH units in the molecule, and benzene has 78/13 or 6CH units in the molecule; and the formulas are, accordingly, acetylene $C_2H_2$, and benzene $C_6H_6$.

The analogy between the calculations in this and the preceeding section should be noted. In Section 122 the number of *elementary* units (atoms) in the molecule is calculated; in this section the number of *compound* units (simplest formulas) in the molecule is calculated. The answer is indicated by a final, completed formula of the molecule.

**124. Dissociation and Molecular Weights.**—Upon heating certain molecules, they dissociate into two or more molecules. As the number of gaseous molecules increases, the volume increases in the same ratio; but as the molecules are lighter, the density decreases. In other words, **substances which dissociate possess abnormal densities and molecular weights at higher tempera-**

**tures.** Lowering the pressure likewise increases the dissociation. The following examples are good illustrations:

(*a*) Iodine vapor is diatomic ($I_2$) up to about 700°, but at 1,700° the molecule is monatomic and the molecular weight and density are reduced to one-half of their normal value:

$$\begin{array}{lcl} I_2\ (700^\circ) & \rightleftarrows & I + I\ (1{,}700^\circ). \\ 254 & & 127 + 127 \\ 1\text{ volume} & & 2\text{ volumes} \end{array}$$

(*b*) Phosphorus pentachloride also dissociates at higher temperatures, yielding phosphorus trichloride and chlorine. Above 300° the dissociation is practically complete:

$$PCl_5 \rightleftarrows PCl_3 + Cl_2.$$

(*c*) When sulfur is vaporized (B.P. 445°), its density varies with changes in temperature. At about 200° and under very low pressure, the molecule is octatomic ($S_8$); and at 800° it is diatomic ($S_2$). Nernst found that 45 per cent of the diatomic molecules are dissociated at 1,900–2,000°:

$$\begin{array}{rcccccc} & 200^\circ & & 800^\circ & & 2000^\circ \\ & S_8 & \rightleftarrows & 4S_2 & \rightleftarrows & 8S. \\ \text{molecular weights} & 256 & & 64 & & 32 \end{array}$$

## QUESTION REVIEW

**Importance of weights (112).**

Why are atomic weights important to the industrialist? Who determines the official atomic weights?

I. THE MASS SPECTROGRAPH (113).

1. What is the principle of the mass spectrograph? Who has contributed most to the study of isotopes?

II. DETERMINATION OF APPROXIMATE WEIGHTS (114).

2. Outline the methods for determining approximate atomic and molecular weights.

**a. Approximate molecular weight of a gas (115).**

3. State Avogadro's law, and show that it is assumed in calculating the approximate molecular weight of any gas.
4. How is the value 22.4 liters arrived at as the gram-molecular volume of any gas?
5. 200 cc. of a gas at 50° C. and 700 mm. weighs 0.8 g. What is its approximate molecular weight?
6. Calculate the weights of 1 liter of each of the following gases at S.T.P.: $CO_2$; $N_2$; $O_2$; air (20% $O_2$, 80% $N_2$); $H_2$; and He. Refer to the table on the inside cover of the text for atomic weights in making your calculations.
7. The atomic weight of chlorine is 35.5. One liter of chlorine weighs approximately 3.2 grams. From these data show that chlorine is diatomic.

**b. Approximate molecular weight of a liquid (116).**

8. 30 cc. of a gas was formed by vaporizing 0.100 g. of a liquid at 100° C. and 750 mm. What is the approximate molecular weight of the substance?

**c. Approximate molecular weight by depression of F.P. (117).**

9. 20 g. of a given solid in 500 cc. of water lowers the freezing point to −3.72° C. What is the molecular weight of the substance?
10. In addition to depression of the freezing point, what other physical properties may be used in determining approximate molecular weights (see section 183)?

**d. Approximate atomic weight from molecular weight × % of element in compound (118).**

11. The weights of 1 cc. of each of 3 gaseous compounds are 0.00115, 0.00076 and 0.0034. They contain a common

element present to the extent of 54.0%, 82.3% and 36.8% respectively. Find the approximate atomic weight of the element.

**e. Approximate atomic weight of a solid from specific heat (119).**

12. What is the approximate atomic weight of a solid which has a specific heat of 0.059? Refer to a table of atomic weights, and try to identify the element.

III. DETERMINATION OF EXACT WEIGHTS.

**a. Exact atomic weights from equivalent weights (120).**

13. 26.97 g. of a given element combines with 24 g. of oxygen. The approximate atomic weight of the substance is 27. What is its exact atomic weight? What is its valence?

**b. Exact molecular weights (121).**

14. What is the exact molecular weight of $CuSO_4, 5H_2O$?
15. A compound containing 92.3% carbon and 7.7% hydrogen has an approximate molecular weight of 25. What is the formula of the compound? What is its exact molecular weight?

IV. MOLECULAR FORMULAS AND WEIGHTS.

**a. Molecular formulas of elements (122).**

16. Calculate the weight of a liter of each of the following gaseous elements: $O_2$, $O_3$, $N_2$, $P_4$.

**b. Molecular formulas of compounds (123).**

17. Three compounds were analyzed and found to contain the following percentages: carbon, 40.00; hydrogen, 6.67; oxygen, 53.33. One liter of the vapor of the first compound weighs 1.3393 g. at S.T.P., and the molar weight of the second is twice that of the first, and that of the third three times that of the second. Find the molecular formulas of the three compounds.

**c. Dissociation and molecular weights (124).**

18. What evidence is there that molecules of sulfur are not diatomic under all conditions?
19. Explain why the molecular weight of phosphorus pentachloride is difficult to measure experimentally.

**Reading References:** Articles number 7, 55, 65, 210, 403 and 423 in the Appendix.

# CHAPTER XII

# COMMON TABLE SALT

## PART I: METALS AND NON-METALS

**125. Industrial Importance of Common Salt.**—Sodium chloride, NaCl, is very abundantly and widely distributed. Salt beds of enormous thickness are found, those at Sperenberg, Germany, reaching a thickness of 4,000 feet. The average thickness of the New York beds is 75 feet, and those of Michigan are, in certain localities, 400 feet thick. There are salt deposits in Galicia, Poland, said to be 50 miles long, 20 miles broad, and 1,200 feet thick. The salt of the Dead Sea supplies a thriving chemical industry in Palestine, and although the sea is only 47 miles long and 9 miles wide, it contains 40 billion tons of salt in solution. It has been estimated that the seven seas contain salt enough to cover the entire dry land to a depth of 400 feet.

Sodium chloride is one of the most important materials in chemical industry. In 1939 the United States produced 8,025,768 short tons of NaCl of which approximately one-quarter was rock salt brought up from mines a mile below the surface of the earth, another quarter came from the evaporation of sea-water, and the remaining half was pumped to chemical factories and sold as brine.

In this and the next chapter we shall study the following chemicals produced from salt on an industrial scale.

NaCl
- Na . . . . . . . . . by electrolysis of molten NaCl (127)
- NaOH . . . . . . by electrolysis of brine (139)
- $Na_2CO_3$ . . . . . soda-ash by the Solvay process (303)
- $Cl_2$ . . . . . . . . . by electrolysis of NaCl (133)
- HCl . . . . . . . . from NaCl plus $H_2SO_4$ (143).

### SODIUM AND METALS

**126. History and Occurrence.**—Sodium was prepared by the electrolysis of molten salt by Sir Humphrey Davy in 1807. The name means "metal of soda," referring to *natron* (an impure, natural sodium carbonate, $Na_2CO_3$, which was used at an early date).

Sodium constitutes about 2.5% of the earth's crust. In addition to its abundance as sea salt and rock salt, sodium is present in Chile saltpeter ($NaNO_3$), and in mineral silicates, borates, carbonates and sulfates.

**127. Preparation of Sodium.**—It is possible to imitate the Davy method of preparing sodium.

### DEMONSTRATION 41. PREPARATION OF SODIUM

Materials: Stick of NaOH, silver or platinum dish, 100 volts D.C., battery clip on one lead, platinum wire on the other; small crystallizing dish.

When a stick of moist sodium hydroxide is placed in a dish which is made the negative pole of a 100-volt current, and the platinum wire, serving as the positive terminal, is brought in contact with the upper part of the stick, a current flows. The sodium hydroxide melts and silvery globules of sodium appear on the dish.

Commercially this process is duplicated by the electrolysis of either fused sodium hydroxide (Castner method) or, more recently, fused sodium chloride (J. C. Downs). In either case sodium appears at the negative pole or cathode.

In the **Castner method** sodium hydroxide is melted at 300° in an iron vessel. When the current is passed, sodium is liberated at an iron cathode and is removed by means of a perforated ladle. Also at the cathode, hydrogen escapes. At the iron anode, oxygen is released.

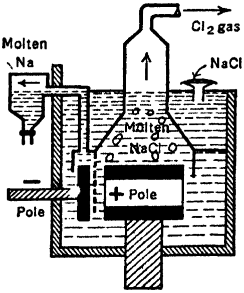
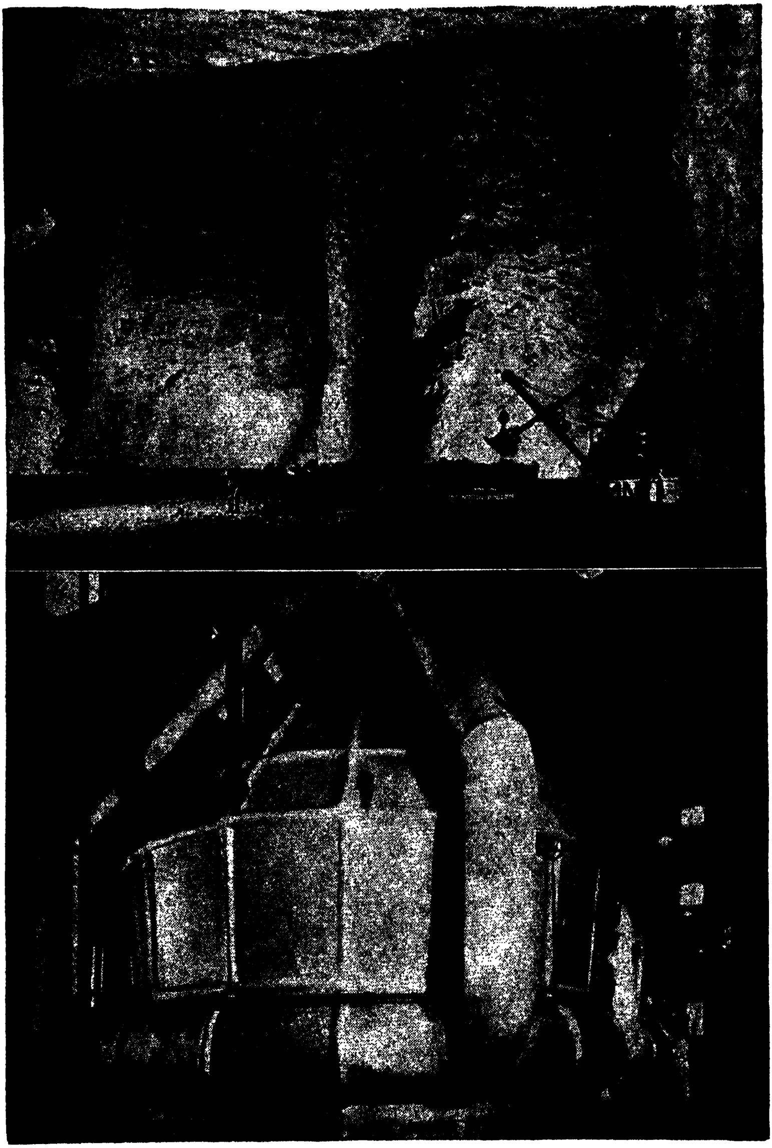


FIG. 61. Downs cell for electrolysis of fused sodium chloride.

The temperature cannot be too high or else the sodium interacts with the sodium hydroxide and is lost:

$$2Na + 2NaOH \rightarrow H_2 \uparrow + 2Na_2O.$$

A **Downs unit** for electrolyzing fused sodium chloride is given in Fig. 61. Solid salt is fed through a hole in the cover of the cell and heated until melted. When the current is passed, chlorine is liberated at the carbon anode, rises through the fused mass and issues from a pipe. Simultaneously sodium is liberated at the iron or copper cathode, and is dis-



*Courtesy of the International Salt Company.*

*Top:* a salt mine.
*Bottom:* evaporators for recovering salt from brine.

charged through another pipe. Pure chlorine and sodium are collected separately out of contact with the air.

**128. Physical Properties of Metals.**—

TABLE 25. ATOMIC AND PHYSICAL PROPERTIES OF SODIUM

| | | | |
|---|---|---|---|
| Symbol | Na | $d_{gas}$ | 12.75 ($H = 1$) |
| At. wt. | 22.997 | $d_{solid}$ | 0.97 |
| At. no. | 11 | B.P. | 880° |
| Electrons | $1s^2\ 2s^2\ 2p^6\ 3s^1$ | M.P. | 97.5° |

DEMONSTRATION 42. PHYSICAL PROPERTIES OF SODIUM AND OTHER METALS

Materials: Lump of sodium, sodium wire, knife; wires of silver, copper, iron and other metals; gold foil, door-bell, dry cell and wires, hammer, sodium press; mirrors of silver, gold, mercury and copper; flask of toluene over burner, test-tube.

Sodium is a soft, malleable, silvery metal. Its luster ordinarily escapes notice, since a fresh surface of sodium quickly tarnishes in air. The white layer of oxides and carbonate may be easily removed by placing the piece of sodium in boiling toluene; the sodium melts and forms a silvery globule which may be poured into a test-tube. **Luster** is a characteristic of metals in general. Silver, aluminum, magnesium and other metals have a white luster, whereas gold is yellow, and copper is red.

A second characteristic physical property of metals is **good conductivity.** The unit conductivity of sodium is exceeded only by that of copper, aluminum, magnesium and gold; but the relative weight per unit conductivity is lower for sodium, because of its lightness, than for any other metal. This electrical conductivity may be demonstrated by touching the wires from a dry cell and door-bell to the ends of a long sodium wire. Sodium wires have actually been used to carry 4,000 ampere currents in lines where a light-weight cable was desirable. Also, since electrical and thermal conductivity are strictly related, the excellent thermal conductivity of sodium has led to its use as a heat transfer medium, such as in cooling airplane motors. Non-metals, in contrast to this, are usually not good conductors.

Metals have a third physical characteristic in common: **malleability and ductility.** Thus gold may be beaten into paper-thin foil; copper may be drawn through dies into tiny wires, and iron may be cold-rolled. The organic chemist utilizes this property of metals by pressing out sodium wire, which he uses to react with and remove traces of water from his organic reagents.

### 129. Chemical Properties of Metals.—

#### DEMONSTRATION 43. CHEMICAL REACTIONS: METALS VERSUS NON-METALS

Materials: Sodium under toluene; sulfur, litmus paper, copper sulfate solution, iron spatula or steel wool, forceps, filter paper, three 400-cc. beakers, deflagrating spoon.

Sodium is near the top of the electromotive series of metals (46) and therefore displaces most of the other metals:

$$\begin{array}{ll} & 2Na + 2HOH \rightarrow 2NaOH + H_2 \uparrow, \\ & 3Na + AlCl_3 \rightarrow 3NaCl + Al \downarrow, \\ \text{just as} & Fe + CuSO_4 \rightarrow FeSO_4 + Cu \downarrow. \end{array}$$

Fresh sodium reacts quickly with oxygen or air, and forms a mixture of oxides, including sodium peroxide, $Na_2O_2$. As is characteristic of oxides of metals, sodium oxide combines with water to form a metallic hydroxide, which turns litmus blue:

$$\begin{array}{ccccc} \text{a metal} & & & & \\ 4Na & + & O_2 & \rightarrow & 2Na_2O \\ 2Na_2O & + & 2H_2O & \rightarrow & 4NaOH. \\ & & & & \text{an hydroxide} \end{array}$$

This is in contrast to the action of non-metals, the oxides of which dissolve in water to form acids (35, *a*).

Sodium forms an **amalgam**, which is an important reducing agent; it interacts with water to form hydrogen. Sodium amalgam is sometimes used instead of pure mercury in the extraction of silver and gold. The amalgam is less active than is sodium alone.

**130. Uses for Sodium.**—Sodium 99.9% pure is used in a number of industries. The DuPont Company in fact has a fleet of freight cars for transporting sodium in 40-ton lots. Its chief use is in the manufacture of sodium cyanide for use in electroplating and in organic reactions. Sodium is used also in the synthesis of certain dyes (*i.e.*, indigo), perfumes (attar of roses), the antiknock compound tetraethyl lead (made by the interaction of ethyl chloride with an alloy of sodium and lead), and in the field of metallurgy for removing antimony from lead. The familiar sodium lamp contains a vapor of mercury and sodium, together with a trace of neon for starting the lamp. When the lamp glows, two intense yellow bands of color, characteristic of sodium, are emitted (300).

### CHLORINE AND NON-METALS

**131. History.**—Scheele, in 1774, treated pyrolusite ($MnO_2$) with hydrochloric acid and liberated a greenish-yellow gas which bleached vegetable colors. He thought it was muriatic (Latin *muria,* brine) acid deprived of phlogiston, and called it "dephlogisticated marine gas." Berthollet (1785) thought that the gas was a compound of muriatic acid and oxygen, or "oxymuriatic acid." Davy (1809–1818) established the elementary nature of the substance, and named it **chlorine** (Greek, *pale green,* or *greenish-yellow*).

**132. Occurrence.**—Chlorine is too active to occur in the free state. Sea salt and rock salt consist mostly of sodium chloride, together with smaller amounts of the chlorides of potassium and magnesium. Horn silver, one of the ores of silver, is AgCl.

**133. Preparation of Chlorine.**—Gaseous chlorine is prepared in the laboratory from HCl plus oxidizing agents; and in industry by electrolysis.

### a. Action of Oxidizing Agents upon Hydrogen Chloride (Laboratory Method)

When $Mn^{+7}$ (as potassium permanganate, $KMnO_4$) or $Mn^{+4}$ (as manganese dioxide, pyrolusite, $MnO_2$) are warmed with concentrated hydrochloric acid, the manganese dioxide acts as an oxidizing agent and removes the hydrogen from HCl, leaving $Cl_2$ gas. In either case the valence of the manganese drops to $Mn^{+2}$:

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2 \uparrow,$$
$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2 \uparrow.$$

A scheme for balancing these equations is discussed below (**134**).

DEMONSTRATION 44. LABORATORY PREPARATION OF $Cl_2$

Materials: Set-up in Fig. 62. 10 g. $KMnO_4$ in the flask; concentrated HCl diluted with one-third its weight of water in the dropping funnel.

When the somewhat concentrated hydrochloric acid is permitted to run slowly from the dropping funnel, and the flask gently warmed, a steady evolution of chlorine occurs. By turning the stop-cock the generation of gas soon stops. The chlorine is freed from HCl by passing through water, and then dried by bubbling through concentrated sulfuric acid. Since chlorine is much heavier than air, it may be collected by upward displacement of the latter.

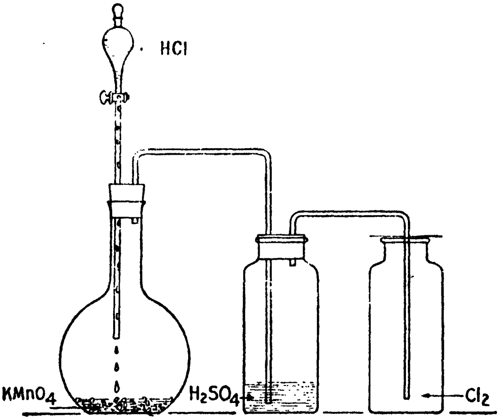


FIG. 62. Laboratory preparation of chlorine.

The method just described is the common laboratory method. Pyrolusite, the mineral form of manganese dioxide, is also used either with concentrated HCl or with a mixture of sodium chloride and concentrated sulfuric acid. (What does this generate?) **Warning.**—*Never mix concentrated sulfuric acid with potassium permanganate; a violent explosion may occur.*

Other higher oxides similar to $MnO_2$, as well as peroxides, yield chlorine when treated with concentrated hydrochloric acid. Note that when some oxides of metals are reacted upon by hydrochloric acid, chlorine is not liberated:

$$MnO + 2HCl \rightarrow MnCl_2 + H_2O,$$
$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O.$$

An important industrial process, now obsolete, for the production of chlorine depended upon the direct oxidation of hydrochloric acid in the gaseous phase at 800° (Deacon's process)

$$4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2.$$

### b. By Electrolysis (Industrial Method)

All the chlorine used commercially in the United States at the present time is produced by the electrolysis of either molten salt or brine:

$$2NaCl_{\text{molten}} \rightarrow 2Na + Cl_2 \uparrow \text{ (Downs)},$$
$$2NaCl_{aq.} + 2H_2O \rightarrow 2NaOH + H_2 \uparrow + Cl_2 \uparrow \text{ (Nelson, Vorce)}.$$

The **Downs cell** was adopted by the United States Government for the manufacture of chlorine at the Edgewood Arsenal during the first World War. 3552 of these cells were installed in the plant, which had a capacity of 110 tons of metallic sodium and 100 tons of chlorine every 24 hours. The two products are kept separated in the cell by a porous diaphragm; the anodes are of carbon. The **Vorce cell** has certain structural advantages over the older Nelson cell. The anodes are of Acheson graphite and are bolted to the copper anode ring; the cathode is a steel screen lined with a diaphragm of asbestos paper. Chlorine is withdrawn into stoneware mains. From the cathode, hydrogen and caustic soda are withdrawn.

### DEMONSTRATION 45. INDUSTRIAL PREPARATION OF $Cl_2$

Materials: Set-up in Fig. 63. Litmus solution. 110 volts D.C.

When brine colored with litmus is electrolyzed, the solution around the anode becomes bleached by the chlorine which is liberated; whereas the cathode turns blue from the presence of sodium hydroxide. This is the chief method for producing chlorine industrially; one plant in West Virginia produces over 200 tons daily.

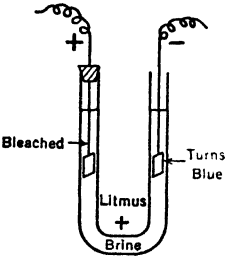


FIG. 63. Electrolysis of brine.

**134. Electron Method of Balancing Equations.**—The equations for the laboratory production of chlorine involve oxidation. There is a special technique for balancing equations of this type; and this will be illustrated for two reactions. See also section 417.

**a. Reaction between Pyrolusite and Hydrochloric Acid**

Step 1.—Write down the reactants and products indicating the substances which change valence:

$$MnO_2 + HCl \rightarrow MnCl_2 + H_2O + Cl_2 \text{ (unbalanced),}$$
$$Mn^{+4} + Cl^{-1} \rightarrow Mn^{+2} + Cl_2^{\circ}$$

Note that chlorine gas has a valence of zero, like any compound (*e.g.*, $Na^{+1}Cl^{-1}$, and $Hg^{+2}O^{-2}$).

Step 2.—Indicate the direction in which electrons have passed, and their number:

$$\underset{\overset{\uparrow}{2e}}{Mn^{+4}} + \underset{\overset{\downarrow}{1e}}{Cl^{-1}} \rightarrow$$

**Step 3.—Increase the number of molecules sufficiently to make the number of electrons lost equal to those gained:**

$$Mn^{+4}O_2 + 2HCl^{-1} \rightarrow$$
$$1 \times 2e = 2 \times 1e$$

Step 4.—Proceed to balance as usual:

$$MnO_2 + 2HCl \rightarrow MnCl_2 + H_2O + Cl_2 \text{ (unbalanced).}$$

Here the $H_2O$ must be increased to $2H_2O$ to take care of the $O_2$ in $MnO_2$. The HCl must be increased by 2HCl to take care of the additional hydrogens. The equation now reads

$$MnO_2 + \underbrace{2HCl + 2HCl} \rightarrow MnCl_2 + 2H_2O + Cl_2,$$

or

$$\mathbf{MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2 \text{ (balanced).}}$$

**b. Reaction between Potassium Permanganate and Hydrochloric Acid**

Step 1.—$KMnO_4 + HCl \rightarrow KCl + MnCl_2 + H_2O + Cl_2$ (unbalanced).
$Mn^{+7} + Cl^{-1} \rightarrow Mn^{+2} + Cl_2^{\circ}$

The student should learn to make intelligent guesses as to the products, rather than memorize. Potassium, for example, might appear as $K_2O$, KOH, or KCl. The first two, however, would react further with the HCl, which is present, to form KCl plus $H_2O$. We are therefore rather sure that KCl is one of the products of the reaction. Again, we have mentioned (133) that manganese will become $Mn^{+2}$ in this reaction; and from the possible products $Mn^{+2}O$, $Mn^{+2}(OH)_2$ and $Mn^{+2}Cl_2$ we should select $MnCl_2$ for the same reasons that we chose KCl. Oxygen and hydrogen would most probably appear as $H_2O$.

Step 2.—
$$\begin{array}{ccc} Mn^{+7} & + & Cl^{-1} \\ \uparrow & & \downarrow \\ 5e & & 1e \end{array}$$

Step 3.—
$$\begin{array}{ccc} 2Mn^{+7} & + & 10Cl^{-1} \\ \uparrow & & \downarrow \\ 2 \times 5e & = & 10 \times 1e \end{array}$$

Step 4.—$2KMnO_4 + 10HCl \rightarrow KCl + MnCl_2 + H_2O + Cl_2$ (unbalanced).

Step 5.—When we attempt to balance this, we find that there is insufficient HCl. This is because the method of electron balancing has taken care only of that Cl which changes into $Cl_2$, and does not account for the chloride ions in KCl and $MnCl_2$ which remain unchanged. We must, therefore, add more HCl to complete the equation:

$$\mathbf{2KMnO_4 + \underbrace{10HCl + 6HCl}_{16\ HCl} \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2 \quad \text{(balanced).}}$$

## 135. Physical Properties of Non-Metals.—

TABLE 26. ATOMIC AND PHYSICAL PROPERTIES OF CHLORINE

| | | | |
|---|---|---|---|
| Symbol | Cl | $d_{gas}$ | 0.00322<br>(about 2.5 times air) |
| At. wt. | 35.457 | B.P. | −33.6° C. |
| At. no. | 17 | M.P. | −102° C. |
| Electronic arrangement | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ | C.T. | +146° C. |
| Isotopes | $^{35}Cl$, $^{37}Cl$ | C.P. | 83.9 atmos. |
| | | Solubility | 215 cc. $Cl_2$ in 100 cc. water at 20° C. |

Chlorine is a greenish-yellow gas possessing a disagreeable smell. When breathed, it has an excessively irritating action upon the membranes of the nose and throat, producing coughing, inflammation, suffocation, and even death.

Because chlorine liquefies at 0° C under only 6 atmospheres of pressure, it was one of the first gases to be liquefied (Northmore, 1806). When a solution of chlorine water is cooled with ice, a greenish-yellow, crystalline **hydrate,** $Cl_2, 8H_2O$, is formed. This hydrate is unstable. Faraday (1823) obtained liquid chlorine by sealing chlorine hydrate in one limb of a strong bent glass tube, and placing that limb in warm water while the other limb was immersed in a freezing-mixture of salt and ice (Fig. 64).

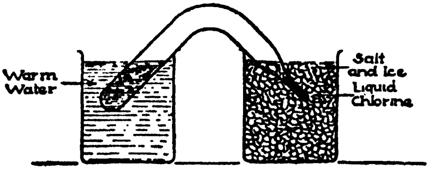


FIG. 64. Liquefaction of chlorine (Faraday).

Faraday, on March 5, 1823, was heating chlorine hydrate in a sealed tube. Dr. J. A. Paris called at his laboratory and observed some oily matter in the tube; he rallied Faraday "upon the carelessness of employing soiled vessels." The experimenter started to open the tube by filing the sealed end, whereupon it exploded and the oily liquid evaporated. The experiment was repeated by Faraday, and the next morning Dr. Paris received the following note:

"Dear Sir,—The *oil* you noticed yesterday turned out to be liquid chlorine.
"Yours faithfully,
"MICHAEL FARADAY."

Faraday carried out more detailed investigations a few years later, and showed that many other gases could be liquefied. In these experiments, he employed a bent glass tube as in the case of chlorine.

The striking contrast between sodium and chlorine well illustrates the differences between metals and non-metals. Sodium, it will be recalled (128), has metallic luster, conducts well, and is malleable and ductile. Chlorine has none of these properties. Neither have any of the other non-metals such as gaseous oxygen or nitrogen, liquid bromine, or solid sulfur, phosphorus or carbon.

**136. Chemical Properties of Chlorine.**—Chlorine is a very active substance, entering into direct combination with many elements and compounds.

### a. Combination with Elements

Chlorine enters into direct combination with most of the elements; oxygen, nitrogen, carbon, argon and the rare gases of the atmosphere are the exceptions.

### DEMONSTRATION 46. CHLORINE AND THE ELEMENTS

Materials: Six jars of chlorine gas, deflagrating spoons, sodium, brass chain, tongs, burner, white phosphorus, antimony powder in a salt-shaker, magnesium ribbon, hydrogen tank with rubber tubing (set-up in Fig. 65).

A jet of hydrogen may be burned in an atmosphere of chlorine and vice versa (Fig. 65).

$$H_2 + Cl_2 \rightarrow 2HCl.$$

When a mixture of hydrogen and chlorine is kept in the dark there is almost no union between the gases at ordinary temperatures; in diffused light, the union is very slow; but when exposed to the light of burning magnesium or to direct sunlight, the mixture explodes at once (Demonstration 74).

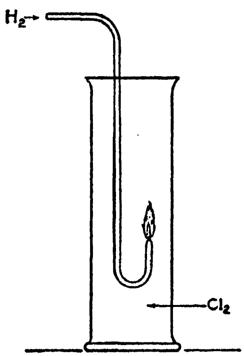


FIG. 65. Combustion of hydrogen in chlorine.

Chlorine combines readily with phosphorus to form $PCl_3$ or $PCl_5$, the latter compound being formed when an excess of chlorine is used.

Chlorine combines readily with all the common metals except gold and platinum. Finely divided antimony, thin leaves of copper or of Dutch leaf (an alloy of Cu and Zn), brass chain and sodium burn in the gas, forming chlorides. Thus:

$$2Sb + 3Cl_2 \rightarrow 2SbCl_3.$$

The combustion of antimony may be shown by sprinkling a little of the powdered metal into a jar of chlorine gas.

When chlorine and the metals are thoroughly dried, they do not combine; but when a trace of water is admitted, combination occurs, the water playing the rôle of a catalyst.

## b. Displacement Reactions

Chlorine is able to displace carbon, iodine, bromine and sulfur from binary compounds.

### DEMONSTRATION 47. DISPLACEMENT WITH CHLORINE

Materials: Chlorine water, two jars of chlorine gas, starch suspension, potassium iodide solution, test tube of turpentine immersed in a beaker of water over a burner, cotton on a wire.

When a very dilute solution of KI is mixed with starch suspension and treated with a drop or two of chlorine water, iodine is liberated and colors the starch blue:

$$2KI + Cl_2 \rightarrow 2KCl + I_2.$$

Also, if a tuft of cotton be dipped into hot turpentine and then thrust into a vessel containing chlorine, the turpentine ($C_{10}H_{16}$) is decomposed with the liberation of so much heat that combustion occurs:

$$C_{10}H_{16} + 8Cl_2 \rightarrow 10C + 16HCl.$$

The cloud of soot (carbon) formed shows that chlorine displaces carbon.

### c. Substitution Reactions

When illuminating gas (methane, marsh gas) is lighted and lowered into chlorine (Fig. 65) a number of reactions occur:

$$CH_4 + Cl_2 \rightarrow HCl + CH_3Cl \quad \text{(methyl chloride)}$$
$$CH_3Cl + Cl_2 \rightarrow HCl + CH_2Cl_2 \quad \text{(methylene chloride)}$$
$$CH_2Cl_2 + Cl_2 \rightarrow HCl + CHCl_3 \quad \text{(chloroform)}$$
$$CHCl_3 + Cl_2 \rightarrow HCl + CCl_4 \quad \text{(carbon tetrachloride)}$$

In each reaction chlorine has **substituted** for hydrogen. Electrovalence, as discussed earlier in this course, obviously does not bind the elements to carbon, for we could not have a positive hydrogen substituting for a negative chlorine.

These are not displacement reactions, for the products are both compounds. They are called **substitution** reactions.

### d. Bleaching and Disinfectant Action of Chlorine

When chlorine is dissolved in water, it interacts with the latter to form hydrochloric and hypochlorous acids:

$$H_2O + Cl_2 \rightleftarrows HCl + HClO.$$

This action is **reversible.** When chlorine water is exposed to sunlight, HClO loses oxygen. Hypochlorous acid is an active oxidizing agent, and is used extensively as a disinfectant and bleaching agent. Chlorine bleaches, therefore, in the presence of water; the bleaching action is really due to the fact that hypochlorous acid is formed, which decomposes, yielding oxygen in an extremely active state:

$$HClO \rightarrow HCl + (O).$$

This (O) combines with dyes forming colorless oxidation products; that is, the oxidized dye is colorless. It kills bacteria by oxidation; that is, the oxidized bacteria are dead.

### DEMONSTRATION 48. BLEACHING ACTION OF CHLORINE

Materials: Two jars of chlorine, one containing some water, the other containing concentrated sulfuric acid; brightly colored cloth, chlorine water, newspaper, pencil and ink drawings.

The bleaching action of chlorine may be shown by lowering moistened strips of highly colored cloth into jars of chlorine. A strip of dry cloth lowered into a cylinder of chlorine standing over concentrated sulfuric acid is not bleached, for the acid in the bottom of the cylinder absorbs the moisture.

Chlorine water bleaches ordinary writing ink (ferrous tannate), but not printer's ink (carbon).

### e. Addition Reactions

Chlorine adds directly to certain compounds. It adds to water forming $Cl_2, 8H_2O$ (**135**).

Again, when a mixture of carbon monoxide and chlorine is exposed to sunlight or heat, $Cl_2$ adds to CO to form carbonyl chloride or **phosgene**:

$$CO + Cl_2 \rightarrow \underset{\text{phosgene}}{COCl_2}.$$

Phosgene is a colorless liquid, boiling at about 8°. It is a highly poisonous substance.

Chlorine also unites with slaked lime, forming bleaching powder:

$$Ca(OH)_2 + Cl_2 \rightarrow \underset{\substack{\text{bleaching}\\ \text{powder}}}{CaOCl_2} + H_2O.$$

**137. Chemical Reactions of Non-metals.**—The reactions of both oxygen (**35–40**) and chlorine (**136**) are typical of the non-metals. They combine with either metals or non-metals to form stable compounds. The more active non-metals displace the less active ones, just as with the activity series of the metals. For the non-metals this activity series is, in order of decreasing activity, F, Cl, O, Br, I. See Demonstration 158. We have already seen (**129**) that oxides of non-metals react with water to form acids, whereas metallic oxides react with water to form hydroxides.

**138. Uses for Chlorine.**—The most extensive use of chlorine is as a **bleaching agent** in the textile and paper industries. Suggested by Berthollet as early as 1785, it became a flourishing industry when the Tennants of Glasgow produced limewater saturated with chlorine, and later chlorinated lime, $CaOCl_2$, for the textile trade in 1795. While it is effective for wood pulp, cotton and linen goods, it is too active for silks and woolens.

The first plant for **treatment of sewage** by chlorine was at Brewster, N. Y., where, in 1893, a plant was erected to protect the New York City water supply at Croton Lake. The nitrogenous matter in the sewage forms chloramine ($NH_2Cl$) which speedily destroys the bacteria. Drinking water today is rendered safe by admixing 2 parts of chlorine per 10,000,000 of water.

To overcome the dangers of gas gangrene during the first World War, Dakin-Carrel developed a solution containing 0.45%–0.50% sodium hypochlorite. Outside of these percentages the solution is either too weak or too irritant. E. O. Sweeney recently invented a portable unit which electrolyzes a solution of salt and sodium bicarbonate to give a fresh **Dakin-Carrel solution** of this exact concentration. The other disinfecting compounds are chloramine-T and dichloramine-T, which likewise chlorinate the micro-organism proteins.

In **medicine**, chlorine is used in hypnotics formed from chloral ($CCl_3CHO$), and in anaesthetics such as chloroform ($CHCl_3$), and ethyl chloride ($C_2H_5Cl$).

Carbon tetrachloride, $CCl_4$, is used in fire extinguishers of the "Pyrene" type. In the dry-cleaning business it is used with other chlorinated organic compounds such as trichlorethylene.

**Great quantities of chlorine and of chlorine compounds were used in the World War.** The first attack was made by the Germans on April 22, 1915. They previously stored the substance in steel cylinders containing 44 pounds each. These were concealed in the trenches, and the substance was employed in the form of gas clouds. As chlorine gas is about 2.5 times as heavy as air, the clouds were carried over the ground by the wind. Chlorine is a powerful respiratory irritant. In high concentration, it affects the eyes also. In a concentration of 1 part of chlorine to 10,000 parts of air, the struggle for breath becomes acute, and a man would probably be incapacitated in 5 minutes.

Some of the most important chlorine compounds used in gas warfare were: *phosgene* ($COCl_2$) *"mustard gas"* ($(C_2H_4Cl)_2S$), and *chloropicrin*, or *nitrochloroform* ($CCl_3NO_2$). Phosgene is chiefly a respiratory irritant, but is more poisonous than chlorine. "Mustard gas" produces serious burns, and in severe cases the larynx, bronchial tubes, and lungs are attacked. Chloropicrin induces coughing, nausea, vomiting, and unconsciousness. Some of the secondary effects are asthma, weak heart, and gastritis.

The Edgewood Arsenal by November 1, 1918 had a total monthly capacity of 1500 tons of chlorine, 1500 tons of chloropicrin, 1050 tons of phosgene, 900 tons of mustard gas, and 90 tons of bromobenzyl cyanide.

## QUESTION REVIEW

**Industrial importance of common salt (125).**

1. State approximately the number of tons of sodium chloride produced from each of its three chief sources.
2. State five industrial products from salt.

I. SODIUM AND METALS.

**a. History and occurrence (126). Preparation of sodium (127).**

3. What is the origin of the word *sodium?*
4. Differentiate the two industrial methods for preparing sodium electrolytically.

**b. Properties of metals (128–129).**

5. State three physical properties commonly possessed by metals. To what practical use is each of these properties put?
6. Discuss displacement reactions in terms of the electromotive series of metals, illustrating with sodium, aluminum, and copper.
7. Compare the chemical behavior of sodium with that of sodium amalgam.
8. What do oxides of all metals form with water?

**c. Uses for sodium (130).**

II. CHLORINE AND NON-METALS.

**a. History (131). Occurrence (132). Preparation (133).**

9. Describe the early discoveries connected with chlorine.
10. Describe the action of oxidizing agents upon HCl.
11. Contrast the Downs and the Nelson methods for preparing chlorine by electrolysis. Which process was demonstrated in lecture?

**b. Electron method of balancing equations (134).**

12. Complete and balance the following equations, using the electron method.

(1) $SnCl_2 + HgCl_2 \rightarrow SnCl_4 + HgCl$
(2) $MnO_2 + H_2SO_4 + NaCl \rightarrow$
(3) $KMnO_4 + H_2O_2 + H_2SO_4 \rightarrow H_2O + O_2 + \cdots$
(4) $FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow Fe^{+3} \cdots$
(5) $MnO_2 + HI \rightarrow$
(6) $KMnO_4 + HBr \rightarrow$

**c. Physical properties of non-metals (135).**

13. State some of the physical properties of chlorine. By what device was it liquefied?
14. Contrast the physical properties of non-metals (oxygen, chlorine) with those of metals (sodium, copper).

**d. Chemical reactions of chlorine: combination, displacement, substitution, bleaching, addition (136).**

15. Which elements do not combine directly with chlorine?
16. Describe a demonstration which illustrates that chlorine is more active than iodine.
17. Why is soot formed when a candle is burned in chlorine?
18. Distinguish between displacement and substitution. What chemical evidence is there that the hydrogen atoms in methane, $CH_4$, are not electrovalent?
19. Give an equation and explain why wet chlorine bleaches, whereas dry chlorine does not.
20. Describe two compounds formed by the combination of chlorine with some other molecules.

**e. Chemical reactions of non-metals (137).**

21. Contrast the chemical reactions of metals with those of non-metals.

**f. Uses for chlorine (138).**

22. Elaborate upon the following uses for chlorine or its compounds: (*a*) bleaching agents; (*b*) treatment of sewage; (*c*) disinfectants; (*d*) fire extinguishers and dry-cleaners; (*e*) war gases.
23. To what use is each of the following put: $CaOCl_2$, $Cl_2$ gas, $NaOCl$, $COCl_2$, $(C_2H_4Cl)_2S$, $CCl_4$, $CHCl_3$?

**Reading References:** Articles number 10, 48, 106, 124, 133, 216, 301, 305, 338, and 344 in the Appendix.

# CHAPTER XIII

# COMMON TABLE SALT

## PART II: HYDROXIDES. ACIDS. SALTS

### SODIUM HYDROXIDE AND METALLIC HYDROXIDES

**139. Preparation of Sodium Hydroxide.**—Sodium hydroxide or **caustic soda, NaOH,** is of great industrial importance. It is produced by two methods.

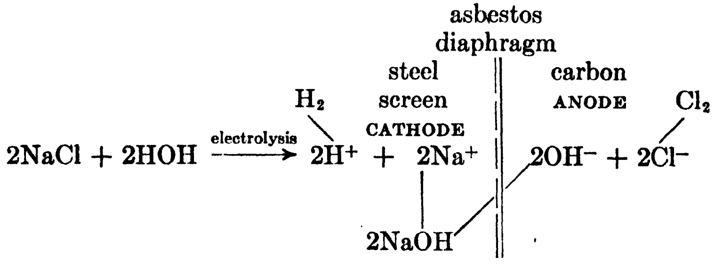
**a. By Interaction of Sodium Carbonate and Calcium Hydroxide**

$$Na_2CO_3 + Ca(OH)_2 \rightleftarrows CaCO_3 \downarrow + 2NaOH.$$

The action is reversible, the best results being obtained when a 10 per cent solution of the carbonate is boiled with lime in an iron vessel. The calcium carbonate may be removed by filtration, and solid sodium hydroxide obtained by evaporation of the filtrate. This method is extensively employed.

**b. By Electrolysis of Sodium Chloride**

The following diagram shows the essential changes which take place when an electric current is passed through the brine. It will be observed that the products are sodium hydroxide, hydrogen and chlorine.

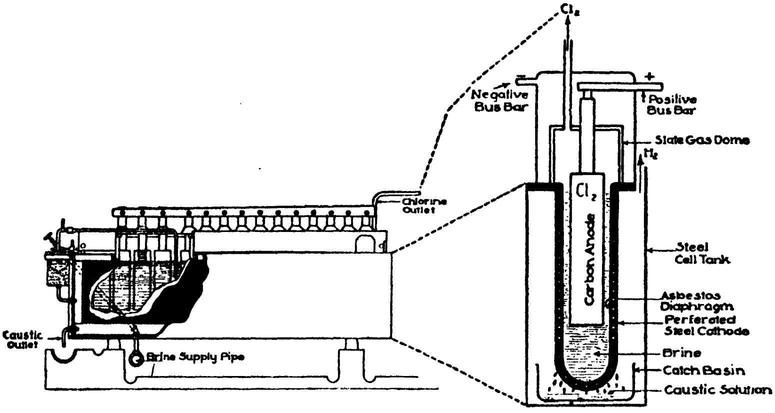


$$2NaCl + 2HOH \xrightarrow{\text{electrolysis}} 2H^+ + 2Na^+ \quad 2OH^- + 2Cl^-$$

**Various cells have been invented to overcome the serious difficulties met with in electrolyzing salt.**

**One of the most successful is the Nelson Cell, which is of the diaphragm type. This means that the products of electrolysis are kept apart by employ-**

ing a porous diaphragm (Fig. 66). The body of the cell is a steel tank having an outlet for the solution of caustic soda. The anodes are constructed of graphite, and are separated from the cathode, a perforated steel plate, by means of a porous diaphragm of asbestos. A saturated solution of sodium chloride is maintained in the anode compartment at a constant level by means of the automatic brine feed. The chlorine gas, which is liberated at the anodes (due to the discharge of the chloride ion), rises through the electrolyte and collects in the slate gas dome, whence it is discharged through a glass pipe. The electrolyte percolates through the asbestos diaphragm to the perforated steel cathode sheet, where hydrogen ion is discharged leaving the hydroxide ion along with the sodium ion. In other words a solution of caustic soda, NaOH, is obtained. This solution, which contains from 10 to 12 per cent of sodium hydroxide, and rather more sodium chloride, is partially evaporated, whereupon the NaCl crystallizes out leaving the more soluble NaOH in solution. By evaporating the caustic solution at a high temperature, sodium hydroxide is obtained and may be cast into sticks.



FRONT VIEW
BATTERY OF CELLS

A SINGLE CELL
IN SECTION

FIG. 66. The Nelson cell for chlorine and sodium hydroxide.

The 3552 Nelson electrolytic cells at the Edgewood Arsenal in 1918 had a capacity of 110 tons of caustic soda and 100 tons of chlorine every 24 hours.

Sodium hydroxide is used on a large scale in the manufacture of soap, for cleansing purposes (lye), in the petroleum industry, and in the manufacture of rayon, paper, textiles, and rubber. The production in the United States is more than 500,000 tons annually.

**140. Physical Properties of Metallic Hydroxides.**—Sodium hydroxide is a white, brittle, deliquescent (68) solid melting at 210°. It is extremely soluble in water, and also in ethyl alcohol.

### DEMONSTRATION 49. PROPERTIES OF HYDROXIDES

Materials: Litmus paper, 10 test glasses with stirring rods; solutions of litmus, phenolphthalein, methyl orange, NaOH, $Ca(OH)_2$, $CuSO_4$, $NH_4OH$, $NiCl_2$, $FeCl_3$, $Zn(NO_3)_2$, and $Al_2(SO_4)_3$.

Hydroxides of sodium, potassium, and ammonium (page 749) are very soluble in water. On the other hand hydroxides of many other metals are insoluble, as may be demonstrated by mixing water solutions of compounds containing these metals with a solution of sodium hydroxide. Double decomposition occurs and insoluble hydroxides precipitate out: $Fe(OH)_3$, brown; $Ni(OH)_2$, apple-green; $Al(OH)_3$, gelatinous white; $Zn(OH)_2$, white; $Cu(OH)_2$, pale blue, and so forth. Many of these hydroxides are formed during the qualitative analysis of a solution containing a mixture of metallic ions.

**141. Chemical Properties of Metallic Hydroxides.**—Concentrated solutions of sodium hydroxide have a corrosive action upon flesh, hence its name, *caustic* soda.

Like many metallic hydroxides, it has a great affinity for carbon dioxide, forming the carbonate, $Na_2CO_3$. A stick of sodium hydroxide soon becomes moist (deliquesces) and coated with sodium carbonate. For this reason it is impossible to weigh out a specified number of grams of *pure* sodium hydroxide in making up a water solution of some fixed concentration. The carbonate may be removed, however, by treatment with barium hydroxide, precipitating $BaCO_3$; or by preparing a very concentrated solution of sodium hydroxide, about 800 grams NaOH per liter of solution. The latter solution will remain pure indefinitely since sodium carbonate is insoluble in it, and precipitates out if the solution is exposed to the air.

Water solutions of sodium hydroxide and other metallic hydroxides turn litmus paper blue. Litmus, phenolphthalein, methyl orange and other indicators turn characteristic colors when a few drops of each are added to solutions of hydroxides. This is due to the common presence of the base $OH^-$ which all of these hydroxides furnish to the solution.

The important reaction between metallic hydroxides and acids to form salts is discussed in detail later (**151**).

## HYDROGEN CHLORIDE AND ACIDS

**142. History and Occurrence of Hydrogen Chloride.**—Hydrochloric acid, a solution of hydrogen chloride in water, was obtained by Glauber, about 1648, by the interaction of common salt and sulfuric acid. Priestley (1772) was probably the first experimenter to collect gaseous hydrogen chloride. He collected the gas over mercury, and named it *marine-acid air*, because it was produced from sea salt.

Hydrochloric acid gas occurs in the gaseous exhalations of certain active volcanoes, especially Vesuvius. Hydrochloric acid is found in the waters of several of the South American rivers which rise in the volcanic districts of the Andes. It is an important component of the gastric juice of man and of animals; the gastric juice of man contains from 0.2 to 0.4 per cent, and that of dogs contains 0.6 per cent.

**143. Preparation of Hydrogen Chloride.**—Hydrogen chloride is formed from the combination of hydrogen and chlorine gas under the influence of light or heat (**136, a; Demonstration 74, section 205**).

Chlorine gas also reacts and removes hydrogen from all its compounds ($H_2S$, $CH_4$, $C_{10}H_{18}$, etc.) with the exception of HF. These are displacement and substitution reactions (**136 b, c**), and result in the formation of hydrogen chloride.

### a. Laboratory Preparation

#### DEMONSTRATION 50. PREPARATION OF HCl

Materials: Set-up in Fig. 62, but set over burner. Sulfuric acid prepared by pouring concentrated $H_2SO_4$ into one-third of its weight of water; concentrated solutions of $NaHSO_4$ and of HCl; test glass.

Common table salt is heated with moderately concentrated sulfuric acid. The HCl which is evolved is heavier than air so that upward displacement of the latter is employed (mol. wt. of HCl = 1. + 35.5 = 36.5; average mol. wt. of gases in the air = 28.95). With an excess of acid, and *gentle* heating, the chemical change is:

$$NaCl + H_2SO_4 \rightleftarrows HCl \uparrow + \underset{\substack{\text{sodium}\\\text{hydrogen}\\\text{sulfate}}}{NaHSO_4}.$$

It should be noted that other chlorides, such as KCl and $NH_4Cl$, can be substituted for NaCl, but the last substance is the cheapest source of both chlorine and hydrochloric acid gas.

Other stable acids with high boiling points might be used instead of $H_2SO_4$ but in practice none is as serviceable as sulfuric acid; for it is cheap, relatively stable, and possesses a high boiling point (338°).

HCl may be dried by passing it through concentrated sulfuric acid.

Note that the above action is reversible. If a concentrated solution of $NaHSO_4$ is treated with concentrated hydrochloric acid, NaCl is precipitated.

### b. Industrial Preparation

The laboratory method just described is the first step in the industrial preparation of HCl. This gas is a by-product in the LeBlanc process for manufacturing sodium carbonate (304), and in the early days of the soda industry the HCl was allowed to escape into the air. As it killed vegetation, manufacturers were required to absorb it in water.

The first action is to heat salt and sulfuric acid in a cast-iron or earthenware pan, forming sodium hydrogen sulfate by the reaction given above. Then the solid bisulfate and more solid sodium chloride are raked into a furnace and heated to a **higher temperature,** completing the second reaction:

$$NaHSO_4 + NaCl \rightleftarrows Na_2SO_4 + HCl \uparrow .$$

The commercial product is often yellow, due to impurities, chiefly ferric chloride.

In essence the laboratory method differs from the industrial only as regards the temperature to which the mixture is heated. The industrialist chooses that temperature which gives him a maximum yield of HCl for a minimum consumption of $H_2SO_4$, the latter being the more expensive ingredient in the process.

$$NaCl + H_2SO_4 \overset{\text{warm}}{\rightleftarrows} NaHSO_4 + HCl \uparrow \text{ (laboratory).}$$

$$2NaCl + H_2SO_4 \overset{\text{hot}}{\rightleftarrows} Na_2SO_4 + 2HCl \text{ (industry).}$$

**144. Properties of Hydrogen Chloride.**—Hydrogen chloride is a colorless gas possessing a sharp odor. It can be condensed to a colorless liquid, the C.T. being 51.4° and the C.P. 81.55 atmospheres. It solidifies to a white crystalline mass, melting at −111.4°. The gas is about 1.25 times as heavy as air. HCl is extremely soluble in water. At 0°, 506 volumes dissolve in 1 volume of water, and at 20°, 442 volumes.

DEMONSTRATION 51. PROPERTIES OF HCl

Materials: Set-up in Fig. 67. The upper flask contains HCl gas generated by heating NaCl with $H_2SO_4$; the lower flask contains water to which a small quantity of blue litmus solution is added. Bottles of concentrated ammonium hydroxide and hydrochloric acid.

A fountain is produced when water is forced from a medicine dropper (Fig. 67) into the upper flask; as hydrogen chloride dissolves immediately, a partial vacuum is produced. External pressure forces water into the upper flask, producing a fountain. Since hydrochloric acid is formed, the litmus solution turns red.

Commercial concentrated hydrochloric acid is water nearly saturated with HCl gas. It contains approximately 37% HCl, and has a specific gravity of 1.19. Upon heating a saturated solution of HCl gas, the liquid loses HCl faster than it does water, and the residual liquid becomes weaker until it finally contains 20.24% HCl. The solution then boils unchanged at 110°, under normal atmospheric pressure. When dilute hydrochloric acid is boiled, it loses water faster than it does HCl. Finally, when the concentration of acid reaches 20.24%, it boils constantly at 110°, yielding a product of constant composition. This is known as a **constant boiling mixture.**

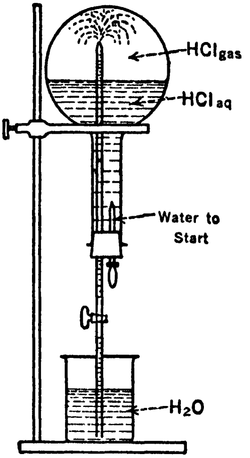


Fig. 67. Fountain produced by a very soluble gas dissolving in water.

The **chemical properties** which hydrogen chloride possesses as a typical acid are given below (146). A specific chemical reaction of some interest in the formation of smoke screens is the reaction between ammonia gas and hydrogen chloride gas to form white clouds of ammonium chloride:

$$HCl + NH_3 \rightarrow NH_4Cl.$$

This may be demonstrated by bringing an open bottle of ammonium hydroxide into proximity with one of hydrochloric acid. (Question: At the mouth of which bottle does the smoke appear? Suggest some explanation.)

**145. Physical Properties of Acids.**—Most 'of our acids are used in the form of aqueous solutions. It may be instructive to examine the physical properties and uses of some of the more common acids. In the instances below, the commercial grade known as **C.P.** (chemically pure) will be described.

**Acetic acid, $CH_3COOH$,** is the acid found in vinegar. **Glacial acetic acid** containing at least 99 per cent acid freezes into an ice-like (hence the name) solid at 16.6° C. Acetic acid is also sold commercially as 30, 36, 60 and 80 per cent solutions in water. This acid is extensively used in dyeing, pharmaceuticals, and in huge tonnage for non-inflammable cellulose acetate fabrics and transparent plastics. The concentration of acetic acid in household vinegar, to conform with the legal standard, is over 4 grams of $CH_3COOH$ per 100 grams of vinegar. As may be surmised from this latter observation, acetic acid must be a very weak acid, or else it could not be used as a food.

**Carbonic acid, $H_2CO_3$,** is an aqueous solution of carbon dioxide gas in water. Soda water and effervescent drinks contain carbonic acid which is unstable, breaking down into water and bubbles of carbon dioxide. Carbonic acid is sold as soda water, and drug stores purchase tanks of carbon dioxide gas for charging their soft drinks.

**C.P. hydrochloric acid,** or muriatic acid, is, as we have seen above, a solution of gaseous hydrochloric acid in water. Hydrochloric acid is used as a solvent; for the preparation of chlorides and chlorine; as a laboratory reagent; in dyeing and calico printing; to clean the surfaces of metals; it is also used in medicine; and it plays an important rôle in digestion.

**C.P. nitric acid,** or aqua fortis, **$HNO_3$,** contains about 70% nitric acid and has a specific gravity of 1.42. Some commercial acid may be yellow due to the presence of oxides of nitrogen formed from the decomposition of the nitric acid. Nitric acid is important in forming nitrocellulose lacquers, nitro-explosives, and in the preparation of nitrates, including fertilizers.

Three volumes of hydrochloric acid mixed with one volume of nitric acid forms a very powerful solution, **aqua regia,** which will dissolve gold and platinum.

**C.P. phosphoric acid,** or orthophosphoric acid, **$H_3PO_4$,** is a syrupy liquid containing 85% acid. It is used chiefly for making phosphates for medicines, fertilizers and foods; and for certain purposes it is replacing sulfuric acid.

**C.P. sulfuric acid,** or oil of vitriol, **$H_2SO_4$,** is an aqueous solution of sulfur trioxide. It has a specific gravity of 1.84, a boiling point of 338°; and although the label on the carboy in which it is sold specifies 98% it generally varies in strength between 94 and 98%. Because its boiling point is considerably higher than most acids, it is used for preparing these acids (**143, a**). Since it is our cheapest acid, it has many uses; and the quantity of sulfuric acid consumed by a country is an index of the chemical industry of that country. **Battery acid** is an especially pure grade of sulfuric acid, free from iron, specific gravity 1.2–1.835, for use in the lead storage battery (**199**).

**146. Chemical Properties of Acids.**—There are many chemical properties which hydrochloric acid shares in common with other acids. This is due to the interaction of all of these acids with water to form the **hydronium ion, $H_3O^+$**:

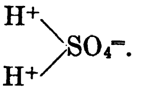
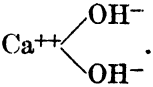
$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$
$$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$$
$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-.$$

NOTE TO TEACHER.—The Brønsted concept of acids and bases is postponed until Chapter XVIII, and may be omitted without breaking the continuity of the text. The term **metallic hydroxide** is consistently used throughout the text, while the term **base** is reserved for the Brønsted concept. According to Brønsted "if the reaction

$$A \rightleftarrows H^+ + B$$

can occur at all, *A* may be called an acid, whatever its charge, and *B* may be called a base, irrespective of the actual stoichiometrical course of the reaction. *A* and *B* form a conjugate pair and are called the **conjugate acid** and its **conjugate base** respectively." Examples:

| the acid | the proton | the conjugate base |
|---|---|---|
| $HCl$ | $\rightleftarrows H^+ +$ | $Cl^-$ |
| $HNO_3$ | $\rightleftarrows H^+ +$ | $NO_3^-$ |
| $NH_4^+$ | $\rightleftarrows H^+ +$ | $NH_3$ |
| $(Al(H_2O)_6)^{+++}$ | $\rightleftarrows H^+ +$ | $(Al(H_2O)_5OH)^{++}$ |
| $HSO_4^-$ | $\rightleftarrows H^+ +$ | $SO_4^{=}$ |
| $HCO_3^-$ | $\rightleftarrows H^+ +$ | $CO_3^{=}$ |

For the present the student should know that acids furnish the hydrogen ion, $H^+$ (or hydronium ion, $H_3O^+$), as in the following examples: $H^+Cl^-$; $H^+NO_3^-$;  $\begin{matrix}H^+\\H^+\end{matrix}\!>\!SO_4^{=}$. On the other hand metallic hydroxides provide the hydroxide ion, $OH^-$, as in the examples: $K^+OH^-$; $Na^+OH^-$; and  $Ca^{++}\!<\!\begin{matrix}OH^-\\OH^-\end{matrix}$.

### DEMONSTRATION 52. CHEMICAL PROPERTIES OF ACIDS

Materials: Dilute acids, hydroxides, salts; 6 test glasses, 5 test-tubes, splint, burner.

Reactions typical of acids ($H_3O^+$) follow.

(*a*) Aqueous solutions of these acids are attacked, with the liberation of hydrogen, by all metals above hydrogen in the

**activity series (46).** The one exception is concentrated nitric acid, which oxidizes the hydrogen to water (**530, c**).

$$\begin{aligned} 2HCl + Mg &\rightarrow MgCl_2 + H_2 \uparrow \\ H_2SO_4 + Zn &\rightarrow ZnSO_4 + H_2 \uparrow \\ 2H_3PO_4 + 3Ca &\rightarrow Ca_3(PO_4)_2 + 3H_2 \uparrow \end{aligned}$$

(*b*) Aqueous solutions of these acids are sour to the taste. This indicates that $H_3O^+$ reacts with and thus affects the taste buds of the tongue.

(*c*) These acids will react (1) with oxides to form water and salts, (2) with hydroxides to form water and salts, (3) with carbonates to form salts, water and carbon dioxide:

$$(1) \left\{ \begin{aligned} 2HCl + FeO &\rightarrow FeCl_2 + H_2O \\ H_2SO_4 + FeO &\rightarrow FeSO_4 + H_2O \end{aligned} \right.$$

$$(2) \left\{ \begin{aligned} HCl + NaOH &\rightarrow NaCl + H_2O \\ H_2SO_4 + 2KOH &\rightarrow K_2SO_4 + 2H_2O \end{aligned} \right.$$

$$(3) \left\{ \begin{aligned} H_2SO_4 + CaCO_3 &\rightarrow CaSO_4 + H_2CO_3 \\ &\qquad\qquad\quad \hookrightarrow H_2O + CO_2 \uparrow \\ 2HNO_3 + Na_2CO_3 &\rightarrow 2NaNO_3 + H_2CO_3 \\ &\qquad\qquad\qquad\quad \hookrightarrow H_2O + CO_2 \uparrow \end{aligned} \right.$$

(*d*) Aqueous solutions of these acids turn litmus pink.

**147. Indicators.**—Litmus is a member of a class of compounds known as **indicators,** which turn one color with acids, another color with hydroxides. Blue litmus forms a pink compound by reacting with the $H_3O^+$ found in all aqueous solutions of acids. Conversely, in solutions of hydroxides, the $OH^-$ removes the $H_3O^+$ from the pink compound, and the litmus reverts to its original blue color. Schematically

$$\begin{aligned} \underset{\text{pink}}{\text{H Litmus}} + H_2O &\rightleftarrows H_3O^+ + \underset{\text{blue}}{\text{Litmus}} \\ \text{H Litmus} + OH^- &\rightarrow H_2O + \text{Litmus}. \end{aligned}$$

Litmus paper is simply paper which has been dyed with litmus solution.

Other indicators act similarly. **Phenolphthalein** turns colorless with acids, deep red with strong hydroxides. A million pounds of phenolphthalein are also used in laxatives and plastics in the United States. An examination of your medicine cabinet may suggest an interesting experiment at home, since phenolphthalein will turn colorless with vinegar, red with washing soda. **Methyl orange** is red with acids, yellow with hydroxides. **Bromcresol-green** is yellow with acids, blue with hydroxides. These are a few of dozens of indicators.

### SODIUM CHLORIDE AND SALTS

**148. Sodium Chloride.**—Common salt, $NaCl$, is important as a food as well as an industrial raw material. The average person consumes 29 pounds of salt per annum in his food; and animals travel long distances to find "salt licks."

Common salt usually contains magnesium chloride, which is very soluble and hygroscopic and therefore causes the salt to "cake" or become wet during humid weather. Starch or sodium bicarbonate is sometimes mixed with salt to prevent its caking. The former covers the particles and the latter interacts with the magnesium chloride to form the insoluble carbonate. Salt may be purified by recrystallization from water solution.

Sodium chloride melts without decomposition at about 800°, and vaporizes at a higher temperature. Its solubility does not increase much with temperature, 35.7 g. of $NaCl$ dissolving in 100 g. of water at 0°.

Common salt crystallizes in transparent cubes, which are occasionally blue due presumably to clusters of free sodium ions within the crystal. We have previously seen (**93, Fig. 49**) that a crystal of sodium chloride does not contain molecules of sodium and chlorine, but rather $Na^+$ and $Cl^-$ ions. Each sodium ion is surrounded by six chloride ions; each chloride ion is surrounded by six sodium ions. We say that the crystal contains an **ionic lattice.** These ions make it possible for salt in water to conduct electricity.

**149. General Solubility Rules for Salts.**—The term **salt is applied to any solid which,** like sodium chloride, **possesses an ionic lattice** in the solid state, and whose water solution conducts electricity. All metallic chlorides, sulfates, nitrates, phosphates, and so forth may be therefore classed as salts. (In the Brønsted system metallic oxides and hydroxides, too, are salts.)

### DEMONSTRATION 53. SOLUBILITIES OF SALTS

**Materials: Eight test glasses, 1 test-tube, burner, solutions containing salts of silver, lead, mercury (ous), barium, copper, calcium, strontium; nitrates, chlorates, acetates, ammonium, sodium, potassium, carbonates, phosphates; dilute hydrochloric, nitric and phosphoric acids.**

The following general rules of solubility for salts should be memorized. Formation of precipitates of the various insoluble salts may be demonstrated with the solutions listed above.

TABLE 27. SOLUBILITIES OF SALTS (page 749)

| **Soluble in water** | **Exceptions** |
|---|---|
| Salts of $Na^+$, $K^+$, $NH_4^+$ | |
| Nitrates and acetates | some basic nitrates and acetates are insoluble. |
| Chlorides, bromides, iodides | $Ag^+$, $Hg^+$ and $Pb^{++}$ salts are insoluble. $PbCl_2$ is slightly soluble in cold, moderately soluble in hot water. |
| Sulfates | $Ba^{++}$, $Sr^{++}$, $Ca^{++}$, $Hg^{++}$ and $Pb^{++}$ sulfates are insoluble. |
| **Insoluble in water. React with dilute acids** | **Exceptions** |
| Carbonates, phosphates | $Na^+$, $K^+$ and $NH_4^+$ salts are soluble. |
| Oxides, hydroxides | $Na^+$, $K^+$, $NH_4^+$, $Sr^{++}$ and $Ba^{++}$ are soluble; $Ca(OH)_2$ is sparingly soluble. |

**150. Formation of Salts.**—Salts may be formed by all four varieties of chemical change, *i.e.*,

*a.* By combination $2Na + Cl_2 \rightarrow NaCl$

*b.* By decomposition $2KClO_3 \rightarrow 2KCl + 3O_2 \uparrow$

*c.* By displacement $Zn + H_2SO_4 \rightarrow H_2 \uparrow + ZnSO_4$

*d.* By double decomposition

$$AgNO_3 + NaCl \rightarrow AgCl \downarrow + NaNO_3.$$

**151. Neutralization and Titration.**—A special case of this latter variety of change is the **reaction between an acid and a metallic hydroxide.** In this case a salt and water are formed. By evaporating off the water, the salt is left. This is a common device for preparing pure salts. Examples:

$$NaOH + HCl \rightarrow H_2O + NaCl \tag{1}$$

$$2NaOH + H_2SO_4 \rightarrow 2H_2O + Na_2SO_4 \tag{2}$$

$$Ca(OH)_2 + 2HNO_3 \rightarrow 2H_2O + Ca(NO_3)_2 \tag{3}$$

$$\text{hydroxide} + \text{acid} \rightarrow \text{water} + \text{salt}$$

The reaction between an acid and an equivalent amount of a metallic hydroxide is called **neutralization**.

### DEMONSTRATION 54. NEUTRALIZATION

Materials: 1 N NaOH, 1 N $H_2SO_4$, phenolphthalein indicator, burette, 400 cc. beaker, stirring rod, 25 cc. pipette. Set-up in Fig. 68.

If 25 cc. of sulfuric acid is run into a beaker half-full of water, and a few drops of phenolphthalein indicator is added, the solution is colorless. This particular indicator is colorless in the presence of the $H_3O^+$ which the acid produces. If, now, sodium hydroxide is run down from burette, and the solution stirred, neutralization takes place according to equation (2) above. If an excess of NaOH is added, the excess $OH^-$ turns the indicator deep red. If, however, the hydroxide is run in carefully, a point can be reached where the correct quantity of NaOH has been added exactly to neutralize the $H_2SO_4$ in the beaker. At this point the addition of a *single* drop of hydroxide will turn the solution from colorless to red. This so-called **titration** is used to determine the relative strengths of acids and hydroxides. For example, by titration with a sodium hydroxide solution of known strength, the acetic acid content of household vinegar may be determined.

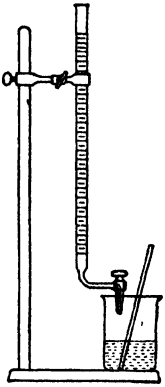


FIG. 68. Apparatus for titration.

## QUESTION REVIEW

I. SODIUM HYDROXIDE AND METALLIC HYDROXIDES.

**a. Preparation of sodium hydroxide** (139).

1. Outline the chemical and the electrical methods for preparing sodium hydroxide.
2. Give the details for the production of sodium hydroxide by the electrolysis of brine.

**b. Physical properties of metallic hydroxides** (140).

3. Name three hydroxides soluble in water, three insoluble in water.

**c. Chemical properties of metallic hydroxides** (141).

4. Why does sodium hydroxide solution become impure when exposed to the air? How may this impurity be removed?

II. HYDROGEN CHLORIDE AND ACIDS.

**a. History and occurrence of hydrogen chloride** (142).

5. How was hydrochloric acid first prepared? Where does it occur in nature?

**b. Preparation of hydrogen chloride** (143).

6. Give an equation illustrating the formation of hydrogen chloride (*a*) by displacement and (*b*) by substitution.
7. Why is sulfuric acid, rather than other acids, used in preparing hydrogen chloride from salt?
8. Differentiate and outline the industrial and laboratory methods for preparing hydrogen chloride from salt.

**c. Properties of hydrogen chloride** (144).

9. Describe an experiment illustrating the solubility of hydrogen chloride gas in water.
10. Explain what is meant by the term "constant boiling mixture."
11. Give an equation showing the formation of smoke screen.

**d. Physical properties of acids** (145).

12. Give the approximate concentrations and some uses for four commercial acids.

**e. Chemical properties of acids** (146).

13. What do all acids form in water? Illustrate by equations in the case of two acids.
14. List four chemical properties of acids which may be attributed to the presence of $H_3O^+$. Give three equations illustrating these.

**f. Indicators** (147).

15. Explain the color changes, in terms of $H_3O^+$ and $OH^-$, which occur with litmus.
16. Name two other indicators, and the colors they turn with acids and hydroxides.

III. SODIUM CHLORIDE AND SALTS.

**a. Sodium chloride** (148).

17. What is the action of starch and of sodium bicarbonate in preventing table salt from becoming sticky?
18. Defend or oppose this statement: "there is no such thing as a *molecule* of sodium chloride."

**b. General solubility rules for salts** (149).

19. State the general solubility rules tabulated in this section. Name three chlorides and three sulfates which are insoluble in water. Three carbonates and three hydroxides which are soluble.

**c. Formation of salts** (150).

20. Give four equations illustrating the formation of salts by the four varieties of chemical change.

**d. Neutralization and titration** (151).

21. Give two equations illustrating neutralization.
22. Give the experimental details for determining the acetic acid content of household vinegar.

**Reading References:** Articles number 48, 106, 124, 301, 305, 338, and 344 in the Appendix.

## CHAPTER XIV

## SOLUTIONS

**152. Types of Solutions.**—Sugar dissolved in water forms what is known as a **solution.** The water is called the **solvent;** while the sugar, which is the substance dissolved in the solvent, is called the **solute.** The molecules of sugar are thoroughly distributed throughout the water, in exactly the same way as the molecules of a gas are distributed throughout the containing vessel.

Water in general has a powerful solvent action on inorganic substances. On the other hand, organic substances dissolve in ether, the alcohols, carbon disulfide, benzene, and carbon tetrachloride. Thus ether is a good solvent for oils and fats, carbon tetrachloride is used in dry-cleaning establishments for dissolving grease, the alcohols dissolve resins, carbon disulfide is a solvent for phosphorus and for sulfur.

The composition of a solution may vary; that is, a solution is a mixture not a compound. Solutions are transparent, but may be colored. For example, a small crystal of potassium permanganate gives a highly colored solution in water.

Exceedingly minute quantities of certain substances have great coloring power. For example, one working with fluorescein dyes may have flecks enough fall into his hair to impart a powerfully fluorescent yellow-green color to the water of a large swimming-pool.

The solute is present in a solution in the molecular form. These particles are so small that they will pass through a filter paper. Thus a small quantity of rosin shaken with alcohol dissolves to form a colorless liquid. This will pass through the pores of a filter paper unchanged, and the rosin may be recovered by evaporating the solution to dryness.

In a muddy stream, it is obvious that not all the solid particles are in solution. Those which are coarse enough will soon settle out. This muddy water is called a **coarse suspension.**

Somewhere between the realm of coarse suspensions, where the particles are so large that they may be seen with the naked eye, and true solutions, where the particles in solution are of molecular dimensions, there is a realm in which the particles consist of clusters of a few thousand molecules. These clusters are still small enough to pass through the pores of a filter paper, and to form a solution which appears transparent. Matter in this state of subdivision is said to be in **colloidal suspension,** forming a **colloidal solution.** When a powerful beam of light is passed through the colloidal solution the presence of the suspended particles is revealed by a Tyndall cone (**668, c**).

### DEMONSTRATION 55. COLLOIDAL SILVER CHLORIDE

Materials: Concentrated HCl, solution of $AgNO_3$, two test-tubes, 1% fresh gelatin solution.

Two drops of concentrated HCl are added to 25 cc. of gelatin solution. A second tube contains two drops of the HCl in 25 cc. of water. Excess $AgNO_3$ added to each tube forms colloidal silver nitrate in the presence of gelatin, and a coarse suspension in the other tube. The colloidal suspension held before a beam of light shows the Tyndall cone, whereas true solutions do not.

Solutions are not restricted to any particular state of matter. Most frequently the word *solution* applies to solutions of solids in liquids; it also applies to liquids and gases in liquids, to gases in gases, and to the three states of matter in solids. Thus, hydrogen is absorbed by palladium and certain other metals, and solid solutions (alloys) of antimony and bismuth are well known. Also, in the field of colloidal suspensions an **emulsion** consists of droplets of one liquid suspended in another: *e.g.*, milk consists of globules of butter-fat floating in a nearly transparent liquid. Cod-liver oil is an emulsion of oil in water. Gelatin with water forms a typical emulsoid solution.

**153. Solution of Gases.**—When two or more gases which do not interact chemically are brought together, they form a homogeneous mixture, which conforms to the definition of a solution. Thus, nitrogen and carbon dioxide are mutually soluble.

When dealing with a mixture or solution of gases, each gas is independent of the others, and the pressure exerted by a gas is called its **partial pressure**; *e.g.*, water at 22° has a vapor pressure of 19.7 mm., and a correction must be made for the partial pressure of aqueous vapor when a gas is measured over water.

While gases are soluble in each other in all proportions, their solubilities in liquids vary, depending upon the nature of the solvent and the gas, as well as upon conditions of temperature and pressure. A liquid may be saturated by bubbling a gas through it until no more gas dissolves.

Some gases are extremely soluble in water, others moderately soluble, and still others only slightly soluble, as shown by the table given below. The solubility is usually expressed in volumes of a gas per 1 volume of the liquid, under given conditions of temperature and pressure.

TABLE 28. SOLUBILITY OF GASES IN 1 LITER OF WATER

| Name of Gas | Volume in Liters Absorbed at 0° and 760 mm. | Volume in Liters Absorbed at 20° and 760 mm. |
|---|---|---|
| Ammonia | 1300 | 710 |
| Hydrogen chloride | 506 | 442 |
| Sulfur dioxide | 79.789 | 39.374 |
| Chlorine | ..... | 2.26 |
| Carbon dioxide | 1.713 | 0.878 |
| Oxygen | 0.049 | 0.031 |
| Nitrogen | 0.0235 | 0.0164 |
| Hydrogen | 0.0215 | 0.0184 |

**154. Effect of Pressure and Temperature upon the Solubility of Gases.**—In 1803 W. Henry enunciated a law governing the solubility of gases.

**Henry's law: At constant temperature, the weight of gas absorbed by a given volume of a liquid is proportional to the pressure at which the gas is supplied.**

This law means that if a liter of water dissolves 5 g. of a gas under 1 atmosphere of pressure, it will dissolve 10 g. under 2 atmospheres.

Henry's law is approximately true for such gases as oxygen and hydrogen; but there are numerous exceptions to the law, due to hydration, reaction with the solvent, or to other causes.

An examination of the table given above shows that gases become less soluble as the temperature rises. It is possible completely to expel air, carbon dioxide, and certain other gases from water by boiling the liquid. This may be shown by boiling water through which $CO_2$ has been bubbled. In the course of a short while, the amount of $CO_2$ escaping falls off, and finally it ceases.

**155. Solution of Liquids in Liquids.**—Under this head there are three cases, namely (1) liquids which mix in all proportions;

*e.g.*, water and alcohol, glycerin and water, sulfuric acid and water; (2) liquids which are practically immiscible: *e.g.*, kerosene and water, benzene and water, mercury and water; (3) liquids which are partially miscible: *e.g.*, ether and water. 100 g. of water dissolves 2.16 g. of ether at 22°, and 100 g. of ether dissolves 11 g. of water.

**156. Solution of Solids in Liquids.**—This is the most common type of solution. The solubility of solids in liquids varies greatly, being dependent upon the nature of the solute, the nature of the solvent, and upon the temperature, but is not much affected by pressure. Although solubility is always limited, it varies within wide limits, as shown by the table below.

TABLE 29. SOLUBILITY OF SOME SOLID SUBSTANCES

| Name of Substance | Grams of Solute in 100 cc. of Water at 18° |
|---|---|
| Silver iodide | 0.00000035 |
| Silver chloride | 0.00016 |
| Barium sulfate | 0.00023 |
| Calcium carbonate | 0.0013 |
| Lead chloride | 1.49 |
| Potassium chlorate | 6.6 |
| Sodium chloride | 35.86 |
| Calcium chloride | 73.19 |
| Silver nitrate | 213.4 |
| Zinc bromide | 478.2 |

The first four substances in the foregoing table are so slightly soluble in pure water that they are called "insoluble." Lead chloride is sparingly soluble in cold water, potassium chlorate moderately soluble, and such solids as silver nitrate and zinc bromide are extremely soluble.

Review the general solubility rules for salts tabulated in Section 149.

**157. Effect of Temperature on the Solubility of Solids in Liquids.**—Change of temperature affects the solubility of a solute. This is shown in Table 30 and in Fig. 69 where solubilities are tabulated and represented graphically by **solubility curves.** It will be observed that in general solids are more soluble in hot water. It will be recalled that the opposite is true for gases, *i.e.*, gases are more soluble in cold water. The

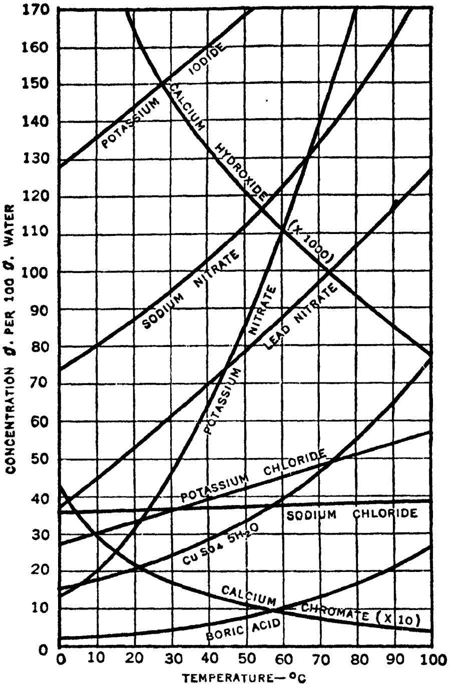


FIG. 69. Solubility curves.

TABLE 30. SOLUBILITY OF SOME COMMON SOLIDS AT DIFFERENT TEMPERATURES

| Substance | Formula | Wt. Dissolved by 100 g. of Water at | | |
|---|---|---|---|---|
| | | 0° | 20° | 100° |
| Barium chloride | $BaCl_2, 2H_2O$ | 31.6 g. | 35.7 g. | 58.8 g. |
| Sodium chloride | $NaCl$ | 35.7 | 36.12 | 39.8 |
| Potassium chloride | $KCl$ | 27.6 | 34.0 | 56.7 |
| Potassium nitrate | $KNO_3$ | 13.3 | 31.6 | 246.0 |
| Sodium nitrate | $NaNO_3$ | 73.0 | 88.0 | 178.0 |
| Potassium chlorate | $KClO_3$ | 3.14 | 7.22 | 56.0 |
| Barium hydroxide | $Ba(OH)_2, 8H_2O$ | 1.67 | 3.89 | 101.4(80°) |
| Boric acid | $H_3BO_3$ | 1.95 | 4.00 | 27.5 |
| Calcium sulfate | $CaSO_4, 2H_2O$ | 0.233 | 0.279(40°) | 0.26(60°) |
| Calcium hydroxide | $Ca(OH)_2$ | 0.185 | 0.165 | 0.077 |

curve for $Ca(OH)_2$ shows that this substance is an exception to the rule, for it is more soluble in cold water.

**Breaks in solubility curves indicate some chemical change in the solute.** Thus, the solubility curve of Glauber's salt, $Na_2SO_4, 10H_2O$, rises quite normally until a temperature of 32.4° is reached; but from this point on the curve slopes downward (Fig. 70). From 0° to 32.4° the decahydrate is in contact with water, but at temperatures above 32.4° $Na_2SO_4$ is present. Glauber's salt, therefore, becomes anhydrous at 32.4°, which is called a **transition point.** We have one solubility curve for the hydrate and a different one for the anhydrous salt:

$$Na_2SO_4, 10H_2O \overset{32.4°}{\rightleftarrows} Na_2SO_4 + 10H_2O.$$

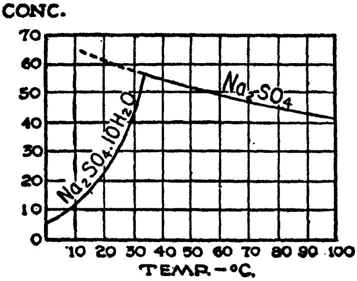


FIG. 70. Solubility curve of Glauber's Salt.

**158. The Law of Partition.**—Carbon disulfide and water are immiscible. That is, if they are poured into a test-tube two separate layers are formed; the carbon disulfide layer is on the bottom. Now, solid iodine is 600 times more soluble in carbon disulfide than in water. It might seem probable, therefore, that if a pinch of iodine is added to a tube containing these two solvents, *all* of the iodine would be dissolved preferentially in the carbon disulfide layer. Such however is not the case. The iodine will distribute itself between the two layers in the ratio of 600 : 1.

### DEMONSTRATION 56. PARTITION OF IODINE

Materials: Two stoppered cylinders, ether, carbon disulfide, iodine, starch solution.

When a small amount of iodine is added to a mixture of water and carbon disulfide, most of the iodine appears in the latter solvent. That some iodine still remains in the water may be proved by adding starch solution to the top layer. In the case of ether and water, where the relative solubility is 200 : 1, the iodine will be distributed in the ratio of 200 : 1 in the two solvents. In this case the colored layer will be on top, since ether is lighter than water.

**Law of Partition (Berthelot and Jungfleisch, 1872): If to two immiscible (or partially miscible) liquids, A and B, a substance be added which is soluble in both, the solute will, if its molecules are identical in both solvents, distribute itself between the two solvents so that the ratio of the concentrations in the two solvents is constant at any particular temperature.**

There are many interesting and important applications of the law of partition, such as the Parkes process for desilvering lead.

**159.—Heat of Solution.**—When a substance goes into solution, heat is either evolved or absorbed. This is called heat of solution.

### DEMONSTRATION 57. HEAT OF SOLUTION

Materials: Concentrated sulfuric acid, ether, 30 cm. of 6 mm. tubing with a small bulb blown on its end, ammonium nitrate, 5 cm. crystallizing dish, 10 cm. square of plywood, matches, test-tube.

The bulb containing ether is placed in a test-tube half-full of water. When concentrated sulfuric acid is poured into the water, the heat of solution is so great that it vaporizes the ether, which may be lighted at the mouth of the tube. The plywood is moistened with a few drops of water and the crystallizing dish nearly full of ammonium nitrate placed upon it. When water is poured upon the ammonium nitrate a result exactly the opposite of the sulfuric acid case is obtained. Heat is absorbed instead of evolved, and to such an extent that the crystallizing dish will be frozen to the plywood.

## CONCENTRATION OF SOLUTE

**160. Molar Solutions.**—The strength of a solution may be conveniently defined in terms of gram-molecular weights. **A molar solution contains 1 mole (gram-molecular weight) of the solute per liter of solution.** Thus, a molar solution of NaCl can be prepared by dissolving 58.46 g. of pure salt in water, and then diluting to a liter. A molar solution of the hydrate *Epsom salt* ($MgSO_4, 7H_2O$) would contain $24.3 + 32 + (4 \times 16) + (7 \times 18.016)$ g. = 246.41 g. per liter. A 2M solution of NaCl will contain $2 \times 58.46$ g. = 116.92 g. of salt per liter of solution. A tenth-molar solution of sodium chloride, written M/10 NaCl, would contain 5.846 g. per liter.

For convenience in preparing solutions of given molarity, so-called **volumetric flasks** are available (Fig. 71). To prepare a one molar solution of NaCl, 58.46 g. of the solid salt is placed in a one liter volumetric flask, water is added, and the flask shaken to dissolve all the solute. When this has been accomplished, additional water is added to bring the total volume of solution up to one liter. Notice that a solution made up in this fashion has not been made by adding 1000 cc. of water to the salt, but that the combined volume of salt plus water is 1000 cc.

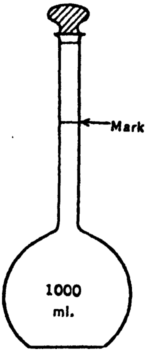


FIG. 71. Volumetric flask.

**We know exactly how many molecules of solute are present in a liter of 1 M solution.** For a gram-molecular weight of any substance contains $6.06 \times 10^{23}$ molecules and this will likewise be the number of molecules of solute present in a liter of 1 M solution.

**161. Normal Solutions.**—A second way to define strength of solution is in terms of its **normality.** This is convenient when we are measuring the volumes of reacting solutions. 10 cc. of a 1 Normal solution of a metallic hydroxide, for example, will exactly neutralize 10 cc. of a 1 Normal solution of an acid. 10 cc.

of a 1 N $KMnO_4$ solution will exactly react with 10 cc. of a 1 N $FeSO_4$ solution.

A normal solution is made up by dissolving

$$\frac{\text{1 gram-molecular weight}}{\text{total valence of the metallic radical}}$$

in water and diluting to 1000 cc. The following table will serve to distinguish between quantities of solute in a 1 N and a 1 M solution.

TABLE 31. MOLAR AND NORMAL SOLUTIONS

| Formula | Molecular Weight | Metal Valence | Grams Solute per 1000-cc. Solution | |
|---|---|---|---|---|
| | | | In 1 Molar | In 1 Normal |
| $Na^{+1}OH$ | 40 | +1 | 40 grams | 40 grams |
| $H_2^{+1}SO_4$ | 98 | +2 | 98 " | 49 " |
| $Al^{+3}Cl_3$ | 133.5 | +3 | 133.5 " | 44.5 " |
| $Na^{+1}HCO_3$ | 84 | +1 | 84 " | 84 " |
| $Al_2^{+3}(SO_4)_3$ | 342 | +6 | 342 " | 57 " |

For example, to make up a 0.1 N $H_2SO_4$ solution, 4.9 grams of $H_2SO_4$ should be present in 1000 cc. of solution. This particular solution would be 0.1 Normal or 0.05 Molar.

**162. Unsaturated, Saturated, Supersaturated Solutions.**—Still a third way to define strength of solution is **in terms of the total solubility of the salt.** For example, when a pinch of salt is covered with water, the molecules dissolve.

If the concentration of the solute is so small that the water is able to dissolve still more salt, we say that the solution is **unsaturated.** Thus, according to Table 30 a solution of salt which at 20° contains only 5 grams of NaCl per 100 g. of water would be unsaturated, by this definition.

If, on the other hand, so much solid salt is added to a beaker of water that not all of it dissolves, and an excess of solid remains on the bottom of the beaker, it is obvious that the water contains as much salt as it can dissolve at that particular temperature. Such a solution is called a **saturated solution,** and is in equilibrium when placed with excess of solute.

$$\underset{\text{(solid)}}{\text{salt}} \rightleftarrows \underset{\text{(dissolved)}}{\text{salt}}$$

For example, a solution containing 36.12 g. of NaCl at 20° is saturated. In terms of the kinetic-molecular theory, particles of salt are passing into the liquid, and an equal number of molecules are returning to the solid and redepositing.

If a given quantity of water is saturated with a certain substance, such as sodium chloride, the liquid can still dissolve other substances. This may be shown readily by shaking a saturated solution of common salt with a colored salt, like copper sulfate or potassium permanganate.

By certain artifices it is occasionally possible to prepare solutions which contain more solute than they normally should. Such solutions are called **supersaturated solutions.** They are in a highly unstable (metastable) condition; they are not in equilibrium with the solute.

### DEMONSTRATION 58. SUPERSATURATION

Materials: 500 cc. Florence flask, cotton, sodium thiosulfate, burner, tripod, wire gauze, sodium chloride crystal.

When sodium thiosulfate (photographer's "hypo"), $Na_2S_2O_3, 5H_2O$, is heated in a clean flask, the salt melts, or dissolves in its own water of hydration. By loosely filling the neck of the flask with clean cotton and then allowing the solution to cool to room temperature, a **supersaturated solution** is obtained, which may be kept for an indefinite period, provided the flask is not disturbed. If the cotton be removed, however, and a minute crystal of "hypo" introduced, crystallization begins at once and salt separates out until a saturated solution is formed at the particular temperature of the liquid. Previous to adding the hypo crystal, it can also be demonstrated that sodium chloride, which belongs to a different crystal system (**91**), cannot serve as a nucleus for relieving supersaturation.

Certain other salts may be used to illustrate the phenomenon of supersaturation: for example, sodium acetate ($NaC_2H_3O_2, 3H_2O$) and Glauber's salt ($Na_2SO_4, 10H_2O$).

A large crystal may be grown by suspending a small crystal of some salt in a saturated solution of the same salt for a few weeks in an open beaker. As water gradually evaporates, saturation is superceded, and the salt comes out of solution.

## COLLIGATIVE PROPERTIES

**163. Physical Properties of Solutions.**—In Section 117 we learned that when certain substances, such as alcohols and sugars, are dissolved in water the water will freeze below 0° C. The amount of lowering depends not upon the chemical properties of the solute, but merely upon the number of solute molecules present in the water. Such a property which is dependent only upon the *number* of molecules is called a **colligative property**. Other colligative properties in which the solution differs from that of the pure solvent are: boiling point, vapor pressure, and a force known as osmotic pressure. These apply to non-aqueous solutions as well as solutions in which water is the solvent.

**164. Lowering of the Freezing Point.**—A mole of such substances as cane sugar ($C_{12}H_{22}O_{11}$), glucose ($C_6H_{12}O_6$), and alcohol ($C_2H_5OH$), when dissolved in 1000 g. of water, lowers the freezing point approximately 1.86°, which is the depression constant for water.

In the case of other solvents, the corresponding value of the depression constant is 5.1 for benzene, 3.9 for acetic acid, and 20.2 for cyclohexane.

The **laws of freezing point depression** state that (1) the depression is proportional to the concentration of the solute (C. Blagden, 1787); and (2) equal numbers of molecules of different solutes in the same quantity of solvent produce equal depressions (F. M. Raoult, 1883). We have already seen (117) how the depression of the freezing point may be used in determining the molecular weight of the solute.

**165. Elevation of the Boiling Point.**—Molecular weights of certain substances may be determined by the boiling point

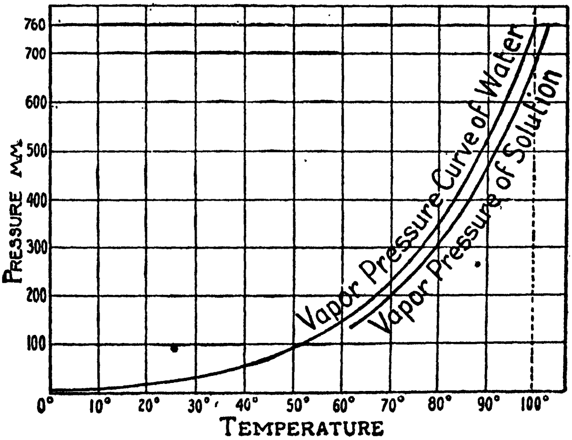


FIG. 72. Vapor pressure of solvent and of solution.

method. **A mole of a substance like sugar, when dissolved in 1000 g. of water, raises the boiling point approximately 0.52°.** The solute interferes therefore with the formation of vapor, so that the vapor pressure curve of the solution is lower than that of the pure solvent (Fig. 72).

The molecular weights of substances which are insoluble in water may be measured by dissolving them in other solvents. The lowering of the F.P. of water we have just seen is 0.52° per mole for water. For benzene as the solvent, the lowering is 2.7°; for carbon tetrachloride as the solvent it is 5.0°.

**166. Lowering of the Vapor Pressure.**—We have just seen that the presence of a solute elevates the boiling point of a solvent. This means that the vapor pressure is lowered. The lowering of the vapor pressure is proportional to the concentration of the solution; it is independent of the chemical properties of the solute, being dependent solely upon the number of molecules.

If with water as a solvent its vapor pressure is lowered below the aqueous tension of the air, **deliquescence** (68) will occur. For in this case more molecules of water reach the solution than escape into the air.

**167. Increasing Osmotic Pressure.**—In 1748, Abbé Nollet showed that if a sugar solution is placed in a vessel closed at the bottom by an animal membrane, and this is dipped into a vessel containing water, the solution will rise in the inner vessel (Fig. 73). This is due to the passage of water molecules through the membrane into the sugar solution, and is evidence of a force which is called **osmotic pressure** (Greek, meaning *impulsion*).

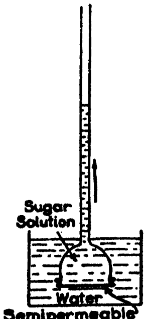


FIG. 73. Osmotic pressure.

DEMONSTRATION 59. OSMOTIC PRESSURE

Materials: Set-up illustrated in Fig. 74. For a semipermeable membrane gold beater's skin, parchment paper, or a hollowed-out vegetable such as a carrot or a beet may be used.

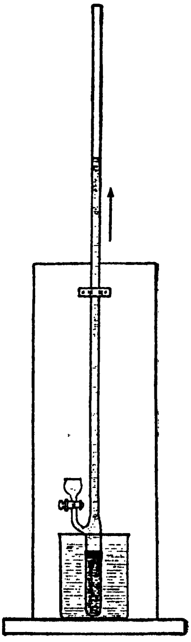


FIG. 74. Osmotic pressure (Dem. 59).

The rise of the liquid in the thistle-tube demonstrates that a pressure is exerted. The column of liquid will rise, if the semipermeable membrane is strong enough, until the hydrostatic pressure so produced is just equal to the osmotic pressure tending to drive the water into the sugar solution.

Careful measurements have established that the **osmotic pressure of a dilute solution is proportional to the concentration of the solute and to the absolute temperature.** Osmotic pressure is somewhat analogous to the gaseous pressure which this substance would exert if it existed as a gas at this same volume and temperature. Laws governing osmotic pressure apply only to very dilute solutions.

### DEMONSTRATION 60. RUPTURED MEMBRANES AND OSMOSIS

Materials: Potassium ferrocyanide, cupric chloride, beaker of water.

7.5 g. of potassium ferrocyanide, $K_4Fe(CN)_6, 3H_2O$, is dissolved in 100 cc. water, and a few crystals of cupric chloride, $CuCl_2$, dropped into the solution. The crystals sink to the bottom, and are soon covered by a thin membrane of cupric ferrocyanide, a reddish-brown insoluble salt:

$$K_4Fe(CN)_6 + 2CuCl_2 \rightarrow Cu_2Fe(CN)_6 \downarrow + 4KCl.$$

This compound serves as a semipermeable membrane, allowing water to pass freely, but preventing the escape of the copper salt. As a consequence, osmosis goes on until fairly large balloon-like forms are to be seen. In case the pressure becomes too great, the membranes are ruptured and then collapse.

Pfeffer (1877) treated porous cylinders with potassium ferrocyanide and a cupric salt so as to fill their pores with cupric ferrocyanide. This formed a diffusion shell strong enough for use in quantitative determinations of osmotic pressure.

In osmosis the pores of the semipermeable membrane are large enough to pass water molecules but too small to pass large molecules such as those of sugar. **This principle is of great importance in assimilation of foods by plants.** When plants grow, water and soluble salts of the soil are taken up by the moist walls of the root-hairs and they circulate through the plants from cell to cell. The salts of nutritive value to the plants interact with the contents of the cells to form complex organic substances which are unable to permeate the membranes of the cells, while the salts of no nutritive value are rejected. Both the rejected salts and water can pass through the membranes in both directions, water circulating more freely. The passage of water and soluble salts into the cells is termed **osmosis.** As the membranes of the cells are permeable to water, but not to the complex substances inside, they are said to be semipermeable. The life of a plant is dependent upon its ability to select from the soil (as well as from the air) those substances required for its growth.

## QUESTION REVIEW

**Types of solutions** (152).

1. Define, also illustrate: solvent, solute, coarse suspension, colloidal suspension, emulsion.
2. How would you distinguish experimentally between a colloidal solution and a true solution?
3. What would you use as a solvent for the following substances: potassium bromide, sulfur, rosin, grease, potassium permanganate?

I. SOLUTION OF GASES (153). EFFECT OF PRESSURE AND TEMPERATURE (154).

4. Define partial pressure. What is the effect of temperature and of pressure upon the solubility of a gas in water? State Henry's law.

II. SOLUTION OF LIQUIDS IN LIQUIDS (155).

5. Illustrate the three cases which may occur when two liquids are mixed.

III. SOLUTION OF SOLIDS IN LIQUIDS (156).

6. Name a solid substance which is insoluble, one which is sparingly soluble, and one which is extremely soluble in water.

a. **Effect of temperature on solubility** (157).

7. Construct solubility curves for potassium chloride, potassium chlorate, boric acid and calcium hydroxide.
8. Explain the significance of a break in a solubility curve. Define transition point.

b. **The law of partition** (158).

9. State the law of partition. Ether is a solvent for butter-fat. Show how the law of partition could be applied to the extraction of butter-fat from milk.

c. **Heat of solution** (159).

10. Describe experiments which show that heat may be either evolved or absorbed when a substance is dissolved in water.

d. **Molar solutions** (160).

11. Describe how a volumetric flask is employed in making up one liter of 1 M NaCl (Na 23, Cl 35.5).
12. What is the molarity of each of the following solutions? (*a*) 37 g. of $Ba(OH)_2, 8H_2O$ in 5 liters of solution, (*b*) 2.45 g. of $H_2SO_4$ in a liter of solution, (*c*) a solu-

tion of HCl containing 39% by weight of HCl and of density of 1.19, (*d*) a 77% solution of $H_2SO_4$ with density 1.7.

13. How many molecules of sodium chloride are there in 1 drop (0.05 cc.) of a 1 M NaCl solution?

**e. Normal solutions (161).**

14. What is the normality of the following solutions: 0.1 M $H_2SO_4$, 2 M $H_3PO_4$, 0.5 M NaCl, 1 M $Al(NO_3)_3$, M/100 $Ca(OH)_2$, M/100 KOH, 0.2 N $NaHCO_3$?

**f. Unsaturated, saturated, supersaturated solutions (162).**

15. How would you prepare a supersaturated solution of a solid substance which was less soluble in hot than in cold water?
16. Define, giving examples, unsaturated, saturated, supersaturated solutions.
17. Describe how you would determine the solubility of sodium chloride in water at some particular temperature. How would you determine the *total solids* in drinking water?

IV. COLLIGATIVE PROPERTIES (163–167).

18. What does the term *colligative properties* mean?
19. Explain deliquescence in terms of the lowering of vapor pressure.
20. Describe two experiments illustrating osmotic pressure.
21. Explain the role of osmotic pressure in plant physiology.
22. If 5 g. of a substance, dissolved in 1000 g. of water, gave a solution freezing at $-0.2°$ C., what is the molecular weight of the substance?
23. Explain why salt will melt ice on a fairly cold day.
24. What is meant by osmosis? Show how osmotic pressure may be demonstrated.
25. Why does calcium chloride allay dust when scattered over roads?
26. What depression in the freezing point of water would be produced by dissolving 20 g. of pure alcohol ($C_2H_6O$) in 1000 g. of water?

**Reading References:** Articles number 75, 208, 301, 403 in the Appendix.

## CHAPTER XV

## IONIZATION

**168. The Arrhenius Theory of Ionization.**—As a result of a study of the properties of aqueous solutions, Svante Arrhenius (1859–1927), a young Swedish chemist, proposed a theory of electrolytic dissociation or **ionization.** He postulated that **the physical and chemical properties of many substances are largely dependent upon their dissociation into electrically charged particles called ions.**

The ions formed by some substances follow.[1]

$$\begin{array}{llll}
 & & \text{Cations} & \text{Anions} \\
HNO_3 & \rightleftarrows & H^+ & + NO_3^-, \\
H_2SO_4 & \rightleftarrows & 2H^+ & + SO_4^=, \\
NaOH & \rightleftarrows & Na^+ & + OH^-, \\
Ca(OH)_2 & \rightleftarrows & Ca^{++} & + 2OH^-, \\
K_2SO_4 & \rightleftarrows & 2K^+ & + SO_4^=, \\
CuCl_2 & \rightleftarrows & Cu^{++} & + 2Cl^-.
\end{array}$$

The experimental evidence which induced Arrhenius in 1883 to propose this startling theory will now be examined.[2] The evidence which Arrhenius presented was threefold: electrical, chemical, and colligative.

**169. Nomenclature of Ions.**—Table 32 illustrates the system employed in naming the various ions as postulated by Arrhenius.

**170. The Nature and Source of Ions.**—Ions carry electrical charges, and these charges correspond to the valences we previously assigned to the various simple and compound radicals.

---

[1] Arrhenius (1883): $HCl \rightarrow H^+ + Cl^-$
Brønsted (1923): $HCl + H_2O \rightarrow H_3O^+ + Cl^-$

Strictly speaking, acids react with water to give the hydronium ion $H_3O^+$, not the hydrogen ion $H^+$. Since this chapter is an historical résumé of the Arrhenius theory, $H^+$ will be used. Undoubtedly, though, the hydrogen ion is hydrated to form the hydronium ion, or even $H_5O_2^+$. If the teacher chooses to present the Brønsted system he will find it in sections 230–237.

[2] Although his studies on colligative properties were not published until 1887, Arrhenius presented the substance of his theory as a doctor's thesis in 1883.

TABLE 32. NOMENCLATURE OF IONS

| Name of Compound | Formula | Name and Formula of Cation | Name and Formula of Anion |
|---|---|---|---|
| Sodium chloride | $NaCl$ | Sodium ion, $Na^+$ | Chloride ion, $Cl^-$ |
| Silver nitrate | $AgNO_3$ | Silver ion, $Ag^+$ | Nitrate ion, $NO_3^-$ |
| Cupric sulfate | $CuSO_4$ | Cupric ion, $Cu^{++}$ | Sulfate ion, $SO_4^{=}$ |
| Ferrous bromide | $FeBr_2$ | Ferrous ion, $Fe^{++}$ | Bromide ion, $Br^-$ |
| Potassium bisulfate | $KHSO_4$ | Potassium ion, $K^+$ | Bisulfate ion, $HSO_4^-$ |
| Ammonium carbonate | $(NH_4)_2CO_3$ | Ammonium ion, $NH_4^+$ | Carbonate ion, $CO_3^{=}$ |
| Calcium hydroxide | $Ca(OH)_2$ | Calcium ion, $Ca^{++}$ | Hydroxide ion, $OH^-$ |
| Chloric acid | $HClO_3$ | Hydrogen ion, $H^+$ | Chlorate ion, $ClO_3^-$ |

Just as the sum of the valences in any compound equals zero, so the sum of the positive and negative ions formed by an ionized substance equals zero. Thus, a water solution of sodium chloride is electrically neutral, inasmuch as it contains an equal number of positive sodium ions and negative chloride ions.

What is the source of the charges on these ions? It will be recalled that our picture of an atom was a central sun surrounded by negative particles of electricity in definite planetary orbits. Sodium, in the presence of chlorine, loses one planetary electron; and the chlorine in turn accepts this electron. The sodium therefore becomes positively charged ($Na^+$), while the chlorine becomes negatively charged ($Cl^-$). It is obvious that by this mechanism an equal number of cations and anions have been formed. This may be represented as follows:

$$NaCl \rightarrow Na^+ + Cl^-.$$

### ELECTRICAL EVIDENCE FOR IONIZATION

**171. Conductivity.**—There are two classes of electrical conductors. **Conductors of the first class** include substances such as metals, alloys, many sulfides (galena, pyrites), and a few nonmetals (carbon). When electricity flows through these substances, they are not changed chemically. Their ability to conduct is associated with the fact that there is free motion of electrons within them; and the passage of the electric current is merely a motion of these electrons.

**Conductors of the second class,** on the other hand, undergo chemical change whenever they conduct electric current. Aqueous solutions of acids, metallic hydroxides, and salts are conductors of the second class. Such substances are called **electrolytes.** Practically all carbon compounds, with the exception of organic acids, bases and salts, do not conduct electricity in aqueous solution; they are called **non-electrolytes.**

Fused, *i.e.*, molten, salts such as AgCl and NaCl, and fused hydroxides such as NaOH and KOH all carry electrical current and are decomposed by it. Dry salts, on the other hand, do not ordinarily conduct.

### DEMONSTRATION 61. CONDUCTIVITY OF ELECTROLYTES

Materials: Set-up shown in Fig. 75; a number of aqueous solutions of acids, metallic hydroxides and salts; HCl in toluene and in water, distilled water, sodium acetate in glacial acetic acid.

The electrical conductivity of a number of electrolytes may be demonstrated. The better the conductor the more brightly will the lamp burn. It will be observed that distilled water is practically a non-conductor; likewise, hydrogen chloride in toluene.

Arrhenius pointed out that the conductivity of electrolytes in water solution is most simply explained by assuming the presence of charged particles to carry the current. This was his first evidence in support of the theory of ionization.

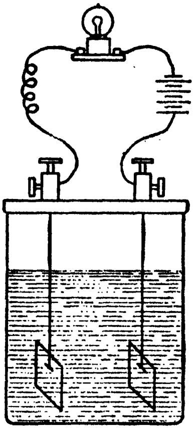


FIG. 75. Illustrating that electrolytes conduct.

**172. Electrolysis.**—While the evidence presented in the preceding section points to the probability of the formation of charged particles, or ions, it indicates nothing as to the positive or negative nature of these ions. This is clearly proven, however, by examining the products formed during the passage of the electrical current (Fig. 76).

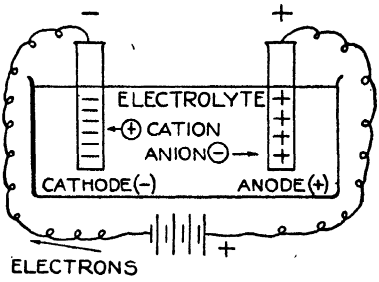


FIG. 76. Electrolysis. Flow of current and of ions.

If a current is passed through **fused sodium chloride,** which is ionized, sodium appears at the negative pole, while chlorine is liberated at the positive pole. This electrolysis of sodium chloride proves that the sodium ion is positively charged and is therefore attracted to the negative pole, while the chlorine is negatively charged and is attracted to the positive pole.

**173. Migration of Ions.**—It is evident that, during electrolysis, ions migrate or move toward the electrodes.

### DEMONSTRATION 62. MIGRATION OF IONS

Materials: Set-up in Fig. 77. A jelly containing cupric sulfate and 5% agar-agar in warm water fills the lower half of the U-tube. A layer of charcoal serves as a boundary line at the surface of the jelly. A solution of potassium nitrate is poured into each limb of the tube. The electrodes lead through a fifty-watt lamp to 110 volts D.C. The tube is immersed in ice and water to dissipate heat generated by the electrolysis.

When the current is turned on, the migration of blue cupric ions ($Cu^{++}$) towards the negative pole is observed. The sulfate ions ($SO_4^{=}$) migrate toward the anode, but cannot be seen since they are colorless. Their presence may be demonstrated by adding a few drops of barium chloride solution just above the charcoal in the positive limb of the tube. White $BaSO_4$ is formed.

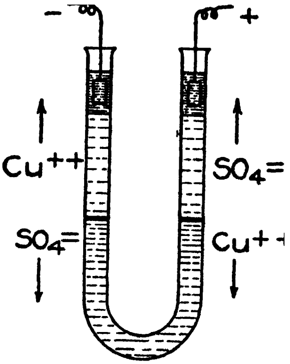


Fig. 77. Migration of ions (Dem. 62).

The **speed of ions**, under given conditions, has been carefully determined by experiment and is different for different ions. Hydronium ion has the greatest speed, and hydroxide ion ($OH^-$) is second.

With electrodes 1 cm. apart, and with a difference of electrical potential of 1 volt between the electrodes of the vessel, the **speeds in centimeters per hour** of a few ions are:

| | | | | | |
|---|---|---|---|---|---|
| $H_3O^+$ | 10.8 | $Na^+$ | 1.26 | $Ag^+$ | 1.66 |
| $OH^-$ | 5.6 | $Cl^-$ | 2.12 | $NO_3^-$ | 1.91 |

**174. Electrical Conductivity and Ionization.**—According to Arrhenius, the extent to which a solution conducts electricity furnishes proof of the extent to which it is ionized. The following experiment serves to illustrate this.

### DEMONSTRATION 63. CONDUCTIVITY AND IONIZATION

Materials: Set-up in Fig. 78. N/10 barium hydroxide, phenolphthalein, 2 N sulfuric acid, milliammeter and dry cell.

When a few drops of phenolphthalein indicator are added to the barium hydroxide, the indicator turns red in the presence of the $OH^-$ ions. Also, the milliammeter shows that the solution is conducting; this is due to $Ba^{++}$ and $OH^-$ ions (the current should be adjusted to give approximately 25 milliamperes when so connected). Sulfuric acid is now added. Immediately, insoluble white $BaSO_4$ is precipitated; but since the $Ba(OH)_2$ is still in excess and provides $OH^-$ ions, the indicator remains red, and the solution conducts electricity. Continue adding sulfuric acid. When exactly enough sulfuric acid to remove all $Ba^{++}$ has been added, the solution ceases to conduct. Also the solution becomes colorless. Why? Neither precipitated barium sulfate nor water furnish many ions to the solution. Upon continuing the experiment, by adding an excess of sulfuric acid, the conductivity of the solution is seen gradually to increase again. Why?

$$Ba^{++} + 2OH^- + 2H^+ + SO_4^{--} \rightarrow BaSO_4 \downarrow + 2H_2O.$$

This puzzling sequence of results can be explained in terms of the Arrhenius theory in a very simple way. It furnishes additional circumstantial evidence in support of the Arrhenius theory.

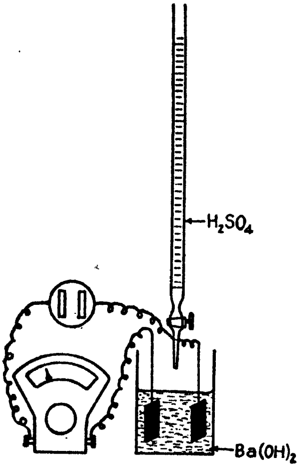


FIG. 78. Electrical conductivity and ionization (Dem. 63).

**175. Electroplating. Faraday's Laws.**—Electroplating is based upon the discharge of cations from salts of metals. Thus, in case of copper salts, the change may be represented as follows:

$$\underset{\substack{\text{Ion}\\ \text{(blue)}}}{Cu^{++}} + 2\ominus \rightarrow \underset{\substack{\text{Metallic}\\ \text{copper}\\ \text{(red)}}}{Cu^0}.$$

Note that cupric ion ($Cu^{++}$) and metallic copper (Cu) are different substances. The former is blue and soluble in water, while the latter is red and insoluble in water.

If a current of 1 ampere is passed through a solution of any silver salt, such as the nitrate, sulfate, or acetate, for one hour, the weight of silver deposited on the cathode is 4.0248 g. The mass of silver is independent, therefore, of the nature of the salt, and it is also independent of conditions, such as temperature, dilution, and current strength. In 1833–4, Faraday expressed this fact as his **First Law of Electrolysis**, which states that **the mass of any substance liberated during electrolysis is proportional to the quantity of electricity passed.**

Actually, this fact is made use of in establishing the **ampere** as a unit quantity of electricity; for an ampere is the quantity of current which will deposit 0.001118 g. silver per second. The quantity of electricity transported past a given point in one second by a current of one ampere is called the **coulomb.**

Faraday was also interested in the amounts of different substances liberated by a given quantity of electricity. He made the startling discovery that 96,500 coulombs of electricity always deposited one gram-equivalent weight of any element (**105**), *i.e.*,

| Element | Weight of Element Deposited by 96,500 Coulombs of Electricity | Equivalent Weight from Chemical Measurements |
|---|---|---|
| Hydrogen | 1.008 | 1.008 |
| Oxygen | 8.000 | 8.000 |
| Silver | 107.88 | 107.88 |
| Chlorine | 35.457 | 35.457 |
| Copper ($Cu^{++}$) | 31.785 | 31.785 |

That there was a relation between electrical units and the chemical units, *i.e.*, coulomb and equivalent weight, was a startling discovery. Faraday expressed this as the **Second Law of Electrolysis,** which states that **the masses of substances liberated by a given quantity of electricity are proportional to their chemical equivalent weights** (Fig. 79).

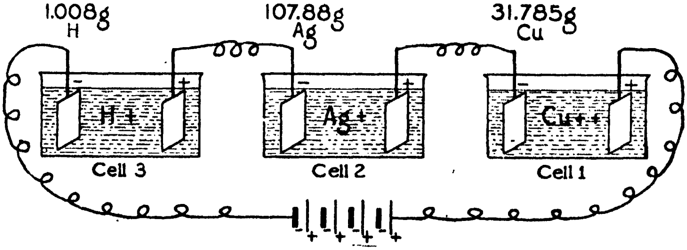


FIG. 79. Faraday's Law illustrated.

The Arrhenius theory explains these two laws simply. The deposition of metals such as sodium, copper and aluminum is represented by the following mechanism:

$$\begin{array}{llll} Na^{+} & +\ 1e & \rightarrow & Na^{0} \\ Cu^{++} & +\ 2e & \rightarrow & Cu^{0} \\ Al^{+++} & +\ 3e & \rightarrow & Al^{0} \\ \text{(ions)} & \text{(electrons)} & & \text{(atoms)} \end{array}$$

From this picture, the first law of electrolysis is self-evident: the more electrons which are passed, the more ions which can be neutralized and deposited out as atoms. The second law is also a consequence of this mechanism. For if a given number of electrons deposit 1 gram-atom of sodium, it will deposit only ½ a gram-atom of copper, and ⅓ a gram-atom of aluminum, inasmuch as it takes 1*e*, 2*e*, and 3*e* to neutralize the three respective metals. This ratio of 1 gram-atom Na : ½ gram-atom Cu : ⅓ gram-atom Al is the same as the equivalent weights of these three metals, since Equivalent Weight = Gram-atomic weight/Valence. Stated in terms of the second law of electrolysis, a given quantity of electricity (for example, 96,500 coulombs, or $6.06 \times 10^{23}$ electrons) will deposit metals in the same ratio as their chemical equivalent weights.

## CHEMICAL EVIDENCES FOR IONIZATION

**176. Color of Ions.**—The colors of various solutions are always associated with the presence of certain ions. Solutions of copper nitrate, chloride, bromide, etc., are usually blue; dichromate solutions are reddish-orange; nickel solutions, green; cobalt solutions, pink; ferric solutions, yellow.

### DEMONSTRATION 64. COLORS OF IONS

Materials: Three test glasses, solid cupric bromide, anhydrous cupric sulfate, solid cupric chloride.

When water is added to the three solid salts, each turns from its original color into a blue solution. In terms of the Arrhenius theory the blue[1] cupric ion $Cu^{++}$ has been formed. The reactions which have occurred are as follows:

$$\underset{\text{brown}}{CuBr_2} \rightarrow \underset{\text{blue}}{Cu^{++}} + 2Br^-$$

$$\underset{\text{white}}{CuSO_4} \rightarrow \underset{\text{blue}}{Cu^{++}} + SO_4^{=}$$

$$\underset{\text{green}}{CuCl_2} \rightarrow \underset{\text{blue}}{Cu^{++}} + \underset{\text{colorless}}{2Cl^-}.$$

This explanation, as you see, involves the Arrhenius assumption that molecules dissociate into ions in water solution.

**177. Common Properties of Acids. Of Hydroxides.**—It has already been pointed out that acids contain hydrogen which may be displaced by magnesium and other metals, and that their aqueous solutions possess a sour taste and turn blue litmus pink. An acid always gives the same reaction independently of the nature of the other constituent, or constituents, of the compound; that is, it contains hydrogen which behaves in a manner essentially different from the hydrogen in such compounds as sugar, alcohol, and hydrocarbons.

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[1] See Jour. Chem. Education 9, 1457 1932. The blue ion is really $Cu(H_2O)_4^{++}$.

It was also pointed out that hydroxides of metals in water solution possess a soapy taste and turn pink litmus blue.

Arrhenius attributed acid properties to the presence of the hydrogen ions, and the properties of hydroxides to the hydroxide ion as shown in the following examples:

| Acids[1] | Hydroxides |
|---|---|
| $HCl \rightarrow H^+ + Cl^-$ | $NaOH \rightarrow Na^+ + OH^-$ |
| $H_2SO_4 \rightarrow 2H^+ + SO_4^{=}$ | $Ca(OH)_2 \rightarrow Ca^{++} + 2OH^-$ |
| $HNO_3 \rightarrow H^+ + NO_3^-$ | $KOH \rightarrow K^+ + OH^-$ |
| etc. $\rightarrow H^+$ | etc. $\rightarrow OH^-$ |

**178. Heat of Neutralization.**—When any of the above acids is added to any of the hydroxides, water and a salt are formed. The reaction is accompanied by an evolution of heat, called **heat of neutralization.** A few heats of neutralization measured by the Danish chemist Julius Thomsen are given below:

$$NaOH + HCl \rightarrow NaCl + H_2O + 13{,}780 \text{ cals.}$$
$$NaOH + HNO_3 \rightarrow NaNO_3 + H_2O + 13{,}780 \text{ cals.}$$
$$KOH + HCl \rightarrow KCl + H_2O + 13{,}780 \text{ cals.}$$
$$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O + 27{,}900 \text{ cals.}$$

At first glance it may appear astonishing that entirely different substances, such as HCl and $HNO_3$, should both give 13,780 calories upon reaction with NaOH. This difficulty is cleared up by the Arrhenius[2] assumption that neutralization is essentially the combining of hydrogen ion with hydroxide ion to form water:

$$\underset{1\text{ g.}}{H^+} + \underset{17\text{ g.}}{OH^-} \rightarrow \underset{18\text{ g.}}{H_2O} + 13{,}780 \text{ cal.}$$

In the case of calcium hydroxide, $Ca(OH)_2$, it will be noticed that 2 molecules of water are formed, so that the quantity of heat liberated is roughly 2 × 13,780 calories.

**179. Rapid Reaction in Water Solution.**—Many reactions which go very slowly in the solid state, take place instantaneously when the solids have previously been dissolved in water, and the solutions are mixed.

---

[1] Brønsted: $HCl + H_2O \rightleftarrows H_3O^+ + Cl^-$
$HNO_3 + H_2O \rightleftarrows H_3O^+ + NO_3^-$

[2] Brønsted: $H_3O^+ + OH^- \rightarrow 2H_2O + 13{,}780$ cal.

### DEMONSTRATION 65. DRY VERSUS WET REACTIONS

Materials: Mortar and pestle, test glass, solids and solutions of mercuric nitrate and of potassium iodide.

The two solids will not react to form red $HgI_2$ until they have been ground together. If the two solutions are mixed, on the other hand, the red precipitate of mercuric iodide appears immediately.

### DEMONSTRATION 66. RAPID REACTION OF IONS

Materials: HCl in toluene, HCl in water, 2 test-tubes, magnesium powder.

The magnesium will not react with hydrochloric acid in toluene, although vigorous reaction occurs in the aqueous solution, and hydrogen is evolved.

In these demonstrations, reactions in the solid state or in toluene take place very slowly. Arrhenius explains the vigorous reaction in water solution by the formation of ions. Hydrogen chloride in toluene is not ionized, whereas hydrogen chloride in water is ionized into $H^+$ and $Cl^-$.

Likewise, when a solution of ammonium carbonate is treated with one of cupric nitrate, a precipitate is formed. The equation for the reaction is essentially as follows:

$$(NH_4)_2CO_3 + Cu(NO_3)_2 \rightarrow 2NH_4NO_3 + CuCO_3 \downarrow .$$

Note that the action takes place at once and without the necessity of heating the substances. Let us contrast with this reaction the one which occurs by heating together in a test-tube dry, solid ammonium carbonate and partially dehydrated cupric nitrate (solid). The reaction takes place slowly at first and becomes more vigorous as the temperature is raised, finally producing a great cloud of gas and smoke. Many different products are formed, such as ammonia ($NH_3$), carbon dioxide ($CO_2$), nitrous oxide ($N_2O$), nitrogen peroxide ($NO_2$), and cupric oxide (CuO). In short, this reaction which occurs in the absence of the solvent water is very complicated, and heat is required; but when solutions of the salts are mixed, the radicals of the factors exchange in a perfectly definite way to form other salts (products).

Again the Arrhenius explanation is that in the dry state ions are not present, whereas in the aqueous solution reaction between ions takes place.

**180. Chemical Analysis.**—The ionic theory simplifies the analysis of solutions of acids, hydroxides and salts; for the detection of these substances is reduced to the identification of their ions. Thus, silver ion is common to all silver salts. This may be detected by adding a solution of a chloride to a solution of a silver salt:

$$Ag^+ + Cl^- \rightarrow AgCl \downarrow .$$

Likewise, addition of barium ion is a test for sulfate ion, which is present in sulfuric acid and in solutions of its salts:

$$Ba^{++} + SO_4^{=} \rightarrow BaSO_4 \downarrow .$$

### DEMONSTRATION 67. CHEMICAL ANALYSIS OF IONS

Materials: Six test glasses, silver nitrate, silver acetate, unknown solution containing silver ion; sodium chloride, potassium chloride; unknown solution containing chloride ion.

Demonstrate how the contents of each solution can be detected by the chemical reactions of ions.

**181. Displacement of Ions.**—From time to time displacement reactions have been discussed (**25**, **45**). For example, when a bright iron spatula is suspended for a few minutes in a solution of copper sulfate, the spatula becomes coated with copper (red):

$$Fe^0 + CuSO_4 \rightarrow FeSO_4 + Cu^0 \downarrow .$$

In terms of ions and electrons, the chemical change may be represented thus:

$$\begin{array}{cccccccc} Fe^0 & + & Cu^{++} & \rightarrow & Cu^0 & + & Fe^{++}. \\ \downarrow & & \uparrow & & & & \\ 2e & = & 2e & & & & \end{array}$$

Since iron is more active than copper, its atom may be regarded as giving two electrons to the copper ion, which is thus transformed into metallic copper.

In a similar manner zinc displaces lead, copper and mercury displace silver (**25**), and active metals displace hydrogen from acids (**45**). The ionic equations for these displacement reactions follow:

$$\begin{array}{lllllll} Zn^0 & + & Pb^{++} & \rightarrow & Zn^{++} & + & Pb^0 \\ Cu^0 & + & 2Ag^{+} & \rightarrow & Cu^{++} & + & 2Ag^0 \\ Mg^0 & + & 2H^{+} & \rightarrow & Mg^{++} & + & H_2^0 \\ \text{more active} & & \text{less active} & & & & \end{array}$$

From this it will be seen that **the more active metal tends to lose electrons,** and thus passes from the elementary state into the ionic condition.

The order of activity of the metals (**45**) gives a series which is often called the **electromotive series** of the metals; for when the electrolysis of normal solutions of their salts is carried out, the electromotive force of the current required to liberate, or deposit, each metal is less than that for any metal preceding it in the series. This means that it requires less difference of potential to deposit such metals as silver and gold than it does to deposit cadmium and nickel.

Likewise **anions may be displaced.** Thus, chlorine displaces iodine from solutions containing iodides:

$$\begin{array}{ccccl} 2I^- & + & Cl_2^0 & \rightarrow & I_2^0 + 2Cl^-. \\ \downarrow & & \uparrow & & \\ 2e & = & 2e & & \end{array}$$

In this case chlorine is a more active non-metal than is iodine, so the iodide supplies electrons to change free chlorine into chloride ions. From this we see that **the more active non-metal tends to gain electrons,** and thus passes from the elementary state into the ionic condition.

### COLLIGATIVE EVIDENCE FOR IONIZATION

**182. Freezing Points of Solutions.**—We have seen that equal numbers of molecules of different solutes in the same quantity of solvent produce equal depressions of the freezing point (117). Now, gram-molecules (moles) of different substances contain the same number of molecules. Table 33 shows the depression of the freezing point of water for several different solutions of equal concentration.

TABLE 33. DEPRESSION OF THE FREEZING POINT OF WATER

| Substance | Formula | Character | Depression Produced by 1 Mole of Substance in 1,000 g. of Water | |
|---|---|---|---|---|
| Alcohol | $C_2H_6O$ | non-electrolyte | 1.85° | normal |
| Dextrose (Glucose) | $C_6H_{12}O_6$ | non-electrolyte | 1.87° | |
| Glycerine | $C_3H_8O_3$ | non-electrolyte | 1.86° | |
| Hydrogen chloride | HCl | acid (electrolyte) | 3.81° | |
| Sodium hydroxide | NaOH | hydroxide (electrolyte) | 3.47° | |
| Sodium nitrate | $NaNO_3$ | salt (electrolyte) | 3.15° | |
| Strontium chloride | $SrCl_2$ | salt (electrolyte) | 5.02° | |

This table shows that 1 mole of a non-electrolyte, such as a sugar or glycerine, dissolved in 1,000 g. of water, lowers the freezing point about 1.86°. This is known as the **molecular depression constant for water.** A mole of an acid, hydroxide, or salt, however, when dissolved in 1,000 g. of water, has an abnormally low freezing point.

In terms of the **Arrhenius theory** the abnormal behavior of electrolytes is quite understandable. Since the depression of the freezing point is proportional to the number of particles, and since electrolytes, according to Arrhenius, dissociate into several particles we should expect the depression to be greater for such electrolytes. This is shown in the following table.

TABLE 34. F.P. DEPRESSIONS (ARRHENIUS)

| Substance | Forms | Number of Particles | Expected F.P. | Observed F.P. |
|---|---|---|---|---|
| 1 molecule of sugar | not ionized | 1 | $-1.86°$ | $-1.86°$ |
| 1 molecule of KCl→ | $K^+ + Cl^-$ | 2 ions | $-3.72°$ | $-3.29°$ |
| 1 molecule of $SrCl_2$→ | $Sr^{++} + 2Cl^-$ | 3 ions | $-5.58°$ | $-5.02°$ |

Disagreement between expected and observed values is attributed to the fact that not all of the molecules have formed free ions in the solution.

**183. Boiling Points and Vapor Pressures of Solutions.**—The vapor pressure (166) of electrolytes is abnormally low. This abnormal lowering of the vapor pressure and raising of the boiling point in the case of electrolytes, indicates that the molecules must have dissociated into several particles in water. The Arrhenius theory postulates that these particles are ions.

Thus we should expect a substance such as $AlCl_3$ to give, theoretically, a four-fold greater elevation of the boiling point than a corresponding amount of sugar, because the latter ionizes into four particles, *i.e.*, $Al^{+++}$ and $3Cl^-$. It will be recalled that these colligative properties depend solely upon the number of solute particles present.

**184. Osmotic Pressures of Solutions.**—The osmotic pressure (167) of dilute solutions is proportional to the concentration (moles per liter) of the solute.

**Solutions of electrolytes exhibit abnormally high osmotic pressures.** Thus, a solution of potassium chloride has an osmotic pressure 1.88 times greater than a corresponding sugar solution; while strontium chloride is 2.7 times greater. These abnormalities are immediately explained by the Arrhenius theory which postulates that KCl forms two ions and $SrCl_2$ forms three ions.

That the osmotic pressures are 1.88 and 2.7 instead of 2 and 3 times normal is explained by the fact that not all of the molecules appear to be ionized.

### DEGREE OF IONIZATION

**185. Arrhenius: Apparent Degree of Ionization.**—The data presented above, and explained rather simply in terms of the Arrhenius theory, lent considerable support to the theory. It is, however, only *qualitative* in nature. In his doctor's thesis, Arrhenius offered *quantitative* evidence as well. The quantitative arguments are based upon the assumption that **not all of the molecules are ionized, that is, there is a certain degree of ionization.** The abnormal behavior of electrolytes as regards chemical reactivity, electrical conductance, and colligative properties has already been taken up. It is evident that those substances which ionize most completely, *i.e.*, which have the greatest degree of ionization, will show the largest abnormalities. Arrhenius recognized this and wrote:

> "The active molecules which are active in regard to electrical properties are also active in regard to chemical properties. I got that idea on the night of the 17th of May 1883, and I could not sleep that night until I had worked through the whole problem. Everything followed from this: the constant amount of heat formed when strong acids and bases react (due to the formation of undissociated water in every reaction of this kind), the reaction of electrolytes (substances which conduct electricity) as being due to the ions first formed, etc."

In his 1883 dissertation Arrhenius presented the material given in Table 35. The methods for obtaining these data will now be described. Before doing this, however, it will be well to illustrate the degree of ionization of a powerful acid, HCl, in contrast with that of a weak acid, $CH_3COOH$ (acetic acid, often written HAc). The extent of ionization is indicated by the relative sizes of the symbols:[1]

$$\small{HCl} \rightleftarrows \large{H^+ + Cl^-}$$

$$\large{HAc} \leftrightarrows \small{H^+ + Ac^-}.$$

**a. Ostwald Chemical Method.**—$H^+$ catalyzes certain chemical reactions. Strong acids, such as HCl, which furnish a larger concentration of hydrogen ions, are more powerful catalysts than weak acids, such as HAc, which furnish

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[1] **Brønsted:**

$$HCl + H_2O \rightleftarrows H_3O^+ + Cl^-$$
$$HAc + H_2O \leftrightarrows H_3O^+ + Ac^-$$

only a small quantity of hydrogen ions. Catalytic activity of these acids will therefore be a measure of their apparent degree of ionization.[1]

**b. Thomsen Neutralization Method.**—We have seen (178) that heat of neutralization of strong acids and hydroxides is approximately 13,780 calories. This is because the essential reaction during neutralization is the combination of $H^+$ and $OH^-$. In the following reaction, for example, $Na^+$ and $Cl^-$ remain as ions at all times:

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow H_2O + Na^+ + Cl^-.$$

For weak acids and hydroxides, where the degree of ionization is small, recombination of ions other than $H^+$ and $OH^-$ are also involved. In this instance the deviation from 13,780 calories is a measure of the apparent degree of ionization.

**c. Arrhenius Conductivity Method.**—As a solution is diluted, the molecules of the solute ionize; and at infinite dilution the solute would be completely ionized. By measuring the electrical conductivity of successively diluted solutions, and extrapolating to infinite dilution, the conduction of a completely ionized solute can be calculated. The conductivity per mole of solute for a more concentrated solution will be less, since not all of the molecules have ionized. The apparent degree of ionization in a concentrated solution, then, is found by dividing the conductivity of the concentrated solution by the conductivity at infinite dilution. This is the experimental method used by Arrhenius in calculating the values in the last column of Table 35.

TABLE 35. APPARENT DEGREE OF IONIZATION

(From the Dissertation of Arrhenius, 1883)

| Acids | OSTWALD (chemical method) | THOMSEN (neutralization) | ARRHENIUS (conductivity) |
|---|---|---|---|
| $HNO_3$ | 100 | 100 | 100 |
| $HCl$ | 98 | 100 | 92 |
| $HBr$ | — | 89 | 86 |
| $HI$ | — | 79 | 92 |
| $H_2SO_4$ | 30–90 | 49 | 48–85 |
| $H_3PO_4$ | — | 13 | 22 |
| HAc | 1.2 | 3 | 8.2 |

Examination of the table shows considerable concordance by the three independent methods. Nitric acid is completely ionized, sulfuric acid is approximately 50% ionized, while only a small percentage of acetic acid is ionized.

**186. Recent Values on Apparent Degree of Ionization.**—Some careful measurements by the conductivity method are listed in Table 36. It will be noticed that water is only slightly ionized, there being only $1H^+$ for every 550,000,000 molecules of water; for this reason water is a very poor conductor of electricity.

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[1] Recent work by Brønsted indicates that the catalysis is often the result of a protolytic reaction (231).

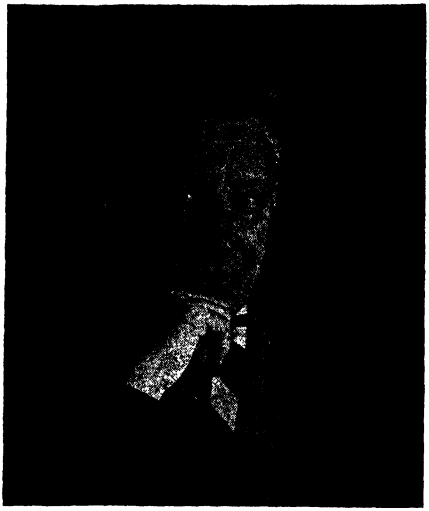
TABLE 36. APPARENT DEGREE OF IONIZATION

(Recent data by conductivity method for 0.1 N solutions at 18° C.)

| Class of substances | Slightly ionized (Weak) 0–2% | | (Medium) 20–90% | | Highly ionized (Strong) 90–100% | |
|---|---|---|---|---|---|---|
| **Acids** | HAc | 1.34 | $H_2SO_4$ | 61 | HCl | 92 |
| | $H_2CO_3$ | 0.17 | | | $HNO_3$ | 92 |
| | $H_3BO_3$ | 0.01 | | | | |
| | $H_2S$ | 0.07 | | | | |
| **Hydroxides** | $NH_4OH$ | 1.3 | $Ba(OH)_2$ | 81 | NaOH | 91 |
| | | | | | KOH | 91 |
| **Salts, etc.** | $Hg^{++}$ compounds | | $ZnSO_4$ | 41 | | |
| | $HgCl_2$ | $<0.01$ | $MgCl_2$ | 73 | | |
| | | | NaCl | 85 | | |
| | | | KCl | 86 | | |
| **Water** | 0.000 000 1 | | | | | |

**187. The Debye-Hückel Theory of Ionization.**—The Arrhenius theory which we have just treated could not explain a number of facts. For example, sodium chloride is 85% ionized in 0.1 M solution at 18° C., according to Arrhenius; *i.e.*, out of every 100 molecules of sodium chloride dissolved in water, 15 of them remain as un-ionized molecules. This is not in agreement with X-ray data, which show that even in the solid state sodium chloride is practically 100% ionized and forms a lattice of sodium ions and of chloride ions (93). This salt dissolved in water would presumably remain in the completely ionized state. Arrhenius must therefore be incorrect in assuming that any of the sodium and chloride ions have recombined to form molecules. Again, what is the source of energy which breaks the molecules into ions in water? Finally, the Arrhenius theory cannot explain how free ions of opposite charge could remain in close proximity without recombining completely to form molecules

In 1923 Debye and Hückel advanced a theory differing radically in some respects from the Arrhenius theory. The precise mathematical formulation of their theory, in which its convincing beauty lies, is unfortunately beyond the scope of this book. It suffices to state that strong acids, hydroxides and salts are practically 100 per cent ionized before dissolving them in water; but that each ion attracts an "**ionic atmosphere**" of opposite charge around it, and forms a cluster with solvent molecules (Fig. 80). Each individual ion is now unable to act as a "**free ion,**" and its mobility is therefore diminished. It may be called a "**bound ion.**" Such bound ions are entirely different, of course,

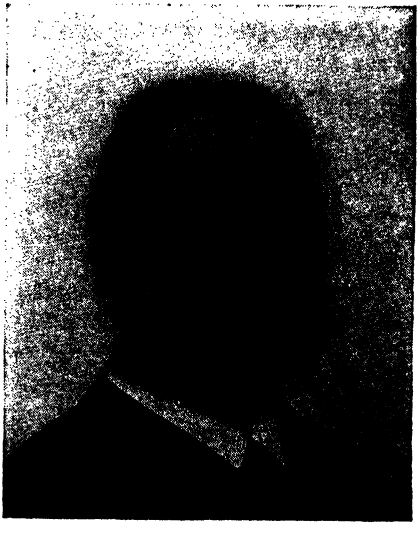


JACOBUS HENRICUS VAN'T HOFF
(1852–1911)

Van't Hoff was born in Amsterdam, and studied at Delft, Leiden, Bonn, Paris, and Utrecht; professor in Amsterdam (1877–1896), and in Berlin (1896–1911); noted for his work on *stereoisomerism*, and for developing some of the great generalizations of modern physical chemistry, as well as for the applications of physical chemistry to geological problems, notably the study of the Stassfurt salt deposits. Van't Hoff was a leading physical chemist of his time.

SVANTE ARRHENIUS
(1859–1927)

Arrhenius was born in Wyk, Sweden; educated in Upsala, specializing in mathematics and physics, and to a less extent in chemistry; propounded in 1883 his celebrated and revolutionary *theory of electrolytic dissociation* (*ionization*); he found adherents in the German chemists, Ostwald and the Dutch chemist, Van't Hoff, with whom he worked; appointed professor in Stockholm (1895), and subsequently Director of the Nobel Institute for Physical Chemistry.



from the Arrhenius concept of "un-ionized molecules"; and yet they explain the same phenomena as Arrhenius' molecules. For example Arrhenius assumes an association of ions to give a neutral molecule, whereas Debye-Hückel assume that every ion is partially associated with, and therefore neutralized by, surrounding ions of opposite charge.

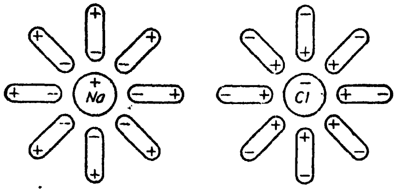


FIG. 80. Ionic atmospheres.

**Debye and Hückel in referring to "apparent degree of ionization" would be referring to the relative freedom permitted the ions by their ionic atmospheres.**

Their theory explains why there is apparently greater ionization in dilute solutions. In this case the more dilute the solution, the farther apart the ions will be; and the more nearly will they be free ions. This is substantiated in Table 37. The mobility of the ion varies inversely as the square root of the concentration.

TABLE 37. VARIATION OF IONIZATION WITH CONCENTRATION

| Concentration (normality) | $(NH_4)NO_3$ | $MgCl_2$ (Fraction apparently ionized) | $MgSO_4$ |
|---|---|---|---|
| 0.001 | 0.987 | 0.941 | 0.850 |
| 0.01 | 0.932 | 0.870 | 0.648 |
| 0.1 | 0.845 | 0.728 | 0.420 |
| 1.0 | 0.704 | 0.545 | 0.245 |

Also, the Debye-Hückel theory indicates that the greater the charge on the ion, the larger the apparent ionic binding, and hence the less the apparent degree of ionization. Thus $Ca^{++}$, $Mg^{++}$, and $SO_4^{=}$ will form compounds with a lower degree of mobility than $Na^+$, $K^+$, and $Ag^+$. This is in agreement with the data in Tables 36 and 37.

The Debye-Hückel theory is highly successful in accounting for the behavior of very dilute solutions of strong electrolytes, but inadequate for concentrated solutions. The Arrhenius theory, while entirely unsatisfactory for all dilutions of strong electrolytes, is nevertheless the basis of the approximate treatment of the behavior of weak electrolytes (*e.g.* acetic acid, ammonium hydroxide).

In conclusion, we may say that the Debye-Hückel theory differs from the Arrhenius theory in that the former recognizes that strong electrolytes are nearly 100% ionized in water solution and that there are no un-ionized molecules there; instead, the "free" ions have become "bound" by taking on an ionic atmosphere which reduces the mobility and activity of the ion. Finally, the two theories are in pseudo-agreement in that the Debye-Hückel theory substitutes "bound ion" for the Arrhenius "un-ionized molecule"; in both cases we have reversible equilibrium between the free ion and the molecule or bound ion; in both cases the substance forms positive and negative ions, which may drag some solvent molecules about with them; in both cases the "degree of ionization" represents the ratio of free ions to bound ions (bound either to form un-ionized molecules, or ionic atmospheres).

**188. Historical Value of the Arrhenius Theory.**—The student may wonder why, if the Arrhenius theory is incorrect, we have bothered to expound it so fully, instead of confining our attention solely to the modern theory of Debye and Hückel. We have done this because the earlier theory marked a milestone along the highway of chemical progress. In 1887 the first volume of the Zeitschrift für Physikalische Chemie, the German Journal of Physical Chemistry, appeared. Its contributors included the young Arrhenius, who showed that colligative properties, as well as the other properties outlined in Table 35, were in accord with his theory. His theory was publicly championed by Ostwald and Van't Hoff, two older chemists whose scientific reputation was international. Arrhenius' postulate that molecules dissociated into charged particles was revolutionary; and for the next twenty years the battle of the ions raged in every chemistry laboratory in the world. Young students flocked to study with Arrhenius, Van't Hoff and Ostwald; and returned home, many to America, to spread the gospel of ions. The "*wild army of ionians*," as they were called, became the leaders of a new generation of chemists; and a branch of chemistry, known as **physical chemistry,** was born. Like most of our scientific theories, the Arrhenius theory was eventually replaced by a newer and more accurate formulation; but not before it had played a rôle of inestimable worth in stimulating and directing chemical research for several decades. For this great service, and as an example of the rise and fall of a typical and important scientific theory, the Arrhenius theory deserves a place in a text such as this.

## QUESTION REVIEW

I. IONIZATION. **Ions and their nomenclature (168–170).**

1. Show how the following substances ionize: $CdSO_4$, $Na_2SO_4$, $Cu(NO_3)_2$, $Ba(OH)_2$. Name the ions.
2. Show the source of the charges in the ions formed from the following substances: $MgCl_2$, $Al_2O_3$ (atomic numbers Mg 12, Al 13, Cl 17, O 8).

II. ELECTRICAL EVIDENCE FOR IONIZATION. **Conductivity (171–174). Migration (173). Electroplating. Faraday's laws (175).**

3. Illustrate conductors of the first and of the second class.
4. Explain what is formed during the electrolysis of molten silver chloride. Why is oxygen evolved during the electrolysis of water?
5. Describe an experiment which shows that ions actually migrate when an electric current is passed. How do you explain the fact that the speed of ions is so slow?
6. Which migrates the faster: the sodium ion or the chloride ion? The silver or the hydroxide ion?
7. A quantity of electricity which liberated 30.5 cc. of hydrogen, measured over water at 20° C. and 765 mm., was also used in the electrolysis of cupric sulfate. Calculate the weight of copper deposited.
8. How many coulombs of electricity would be required to deposit, or liberate, a gram-atomic weight of each of the following elements: hydrogen, oxygen, chlorine, zinc, silver, iron ($Fe^{++}$), and copper ($Cu^{++}$)? Explain

III. CHEMICAL EVIDENCE FOR IONIZATION. **Color (176). $H^+$ and $OH^-$ (177). Heat of neutralization (178). Rapid reaction (179). Analysis (180). Displacement (181).**

9. Explain why three different colored copper salts will all turn blue when dissolved in water.
10. Explain the fact that acids have similar properties.
11. How many calories are evolved upon neutralizing aluminum hydroxide with sulfuric acid?
12. What chemical experiment illustrates that hydrogen chloride in toluene is not ionized?
13. How many different salts could be formed by the union of 10 different cations with 10 different anions? In the identification of these salts by chemical tests, how many different kinds of tests would be necessary?
14. If a solution containing salts of zinc, copper and magnesium is electrolyzed, in what order will the metals plate out?

15. Indicate by an equation how electrons are passed during the displacement of lead by zinc; of hydrogen by magnesium; of bromine by chlorine.

IV. COLLIGATIVE EVIDENCE FOR IONIZATION. **Freezing point. Boiling point. Vapor pressure. Osmotic pressure. (182–184.)**

16. Define the words *colligative properties.* Name four colligative properties.
17. Explain why a mole of strontium chloride lowers the freezing point of 1,000 grams of water 5.02°, whereas a mole of sugar will lower it only 1.86°.
18. Which is more efficient, a kilogram of methyl alcohol, of cane sugar, or of table salt as an anti-freeze in automobiles? Look up formulas and atomic weights.

V. DEGREE OF IONIZATION.

a. **Arrhenius: apparent degree of ionization (185–186).**

19. Describe the three independent methods which Arrhenius employed in his doctor's thesis as evidence of apparent degree of ionization.

b. **Debye-Hückel theory versus Arrhenius theory (187–188).**

20. What is known about the ionization of such salts as NaCl and KCl, both in the solid state and in aqueous solution? What is supposed to be the source of the ionic charges?
21. How, according to the Debye-Hückel theory, does the percentage of bound ions depend upon the charge of the ion, as for example $Ca^{++}$ versus $Na^{+}$, or $SO_4^{=}$ versus $NO_3^{-}$?
22. Why should an obsolete theory, such as that of Arrhenius, be taken up in this text?

**Reading References:** Articles number 75, 301, 403, 420 and 423 in the Appendix.

## CHAPTER XVI

## ENERGY AND CHEMICAL CHANGE

**189. Transformations of Energy.**—The word energy is derived from the Greek, meaning *"in work."* According to Ostwald, **energy is work and all else that can arise from work and be converted into work.** In our coal and petroleum deposits there are great stores of energy or possible work. This is called **potential energy.** A stone raised above the surface of the earth possesses potential energy. In falling, it can do work.

A body in motion, on the other hand, is said to possess **kinetic energy.** Examples of this type of energy are a moving projectile, rushing water, fuel undergoing oxidation, explosions. In the last two examples, molecules are colliding and breaking up to form new molecules.

The various forms of energy are interconvertible. For example, the motion of the water at Niagara Falls is converted into **electrical energy**; this in turn may be converted into **light energy** or into heat or **thermal energy,** or transformed in a motor back into the energy of motion, **mechanical energy.**

Throughout all of these transformations of energy nothing has been destroyed. Formulated as the **Law of Conservation of Energy,** this may be stated as: **Energy is neither created nor destroyed, although it may be transformed into any of the forms of which energy is susceptible.** This law of physics is the counterpart of the chemical Law of Conservation of Mass (**102**). We shall see later (**258**), however, that in certain cases even matter and energy are interconvertible; that at the tremendous temperatures of the stars, energy may be converted into material substance, while the material destroyed during the conversion of hydrogen into helium in the sun releases enough energy to keep that body hot.

**190. Potential Energy Curves of Molecules.**—In 1926 a new branch of mathematics known as **quantum mechanics** was developed to express the energies which exist within atoms. Without delving into this elaborate mathematics we shall summarize the conclusions furnished by its application.

Let us assume that two electrons (*i.e.*, two negative charges) are brought together. Consider the forces involved. A plot of the energy of this system against the distance between the two electrons is given in Fig. 81; for according to the laws of physics the repulsive force between two like charges varies inversely as the square of their distance.

Next, let us bring two hydrogen atoms together. This case is not as simple as the preceding one because there is not only the repelling force of the two hydrogen nuclei, but an attractive force between the electrons of each hydrogen atom and the nucleus of the other. The magnitude of this so-called **interaction** between the various negative and positive charges in any two atoms brought together in this fashion may be calculated by the use of quantum mechanics. For two hydrogen atoms the total forces so calculated are shown in Fig. 82. Still another curve, in this case for two neon atoms, is shown in Fig. 81.

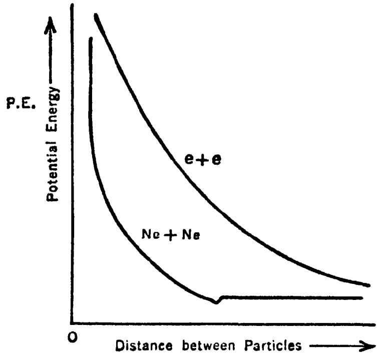


FIG. 81. Potential energy curves. Forces involved in bringing two electrons or two neon atoms together.

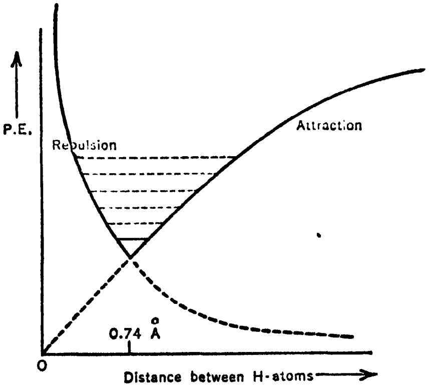


FIG. 82. Potential energy curve for two hydrogen atoms.

The physical significance of these figures reveals an interesting prediction by the use of quantum mechanics. In the case of hydrogen there is a critical distance, 0.74 Ångstroms, *i.e.*, $0.74 \times 10^{-8}$ cms., where the potential energy, P.E. of the system is at a minimum. Physically, this means that when two hydrogen atoms are 0.74 Ångstroms apart they cannot be separated unless a certain amount of energy is supplied. In other words, the hydrogen molecule, from potential energy considerations, is diatomic. On the other hand, there is no such trough in the neon curve; that is, there is no tendency for two neon atoms to remain together. This too is in accord with the fact that the neon molecule is monatomic.

**191. Potential Energy Curves for Chemical Reactions.**—Potential energy curves may also be constructed to show the forces involved during a chemical reaction (Figs. 83–84). P.E. is the summation of all the interaction forces of the different atoms entering into the reaction; and the abscissa is a function of the distances between these atoms. In general we shall consider point A as the potential energy of the system *before* reaction, and point B the potential energy *after* reaction.

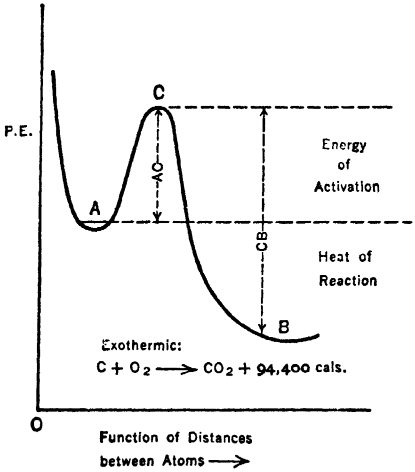

P.E.
C
A
AC
CB
Energy of Activation
Heat of Reaction
B
Exothermic:
$C + O_2 \longrightarrow CO_2 + 94,400$ cals.
O
Function of Distances between Atoms →

FIG. 83. Potential energy curve for an exothermic reaction.

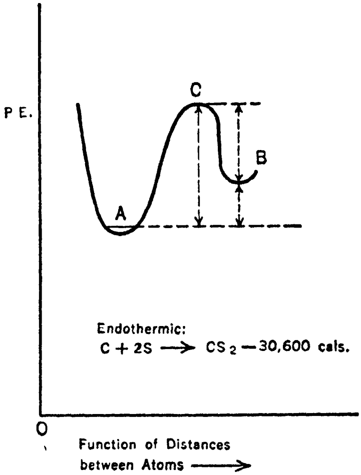

P E.
C
B
A
Endothermic:
$C + 2S \longrightarrow CS_2 - 30,600$ cals.
O
Function of Distances between Atoms →

FIG. 84. Potential energy curve for an endothermic reaction.

Let us examine the curve for the oxidation of carbon. Before the system can change from A to B it is necessary to supply some energy to take it over the potential energy hump. This corresponds with our common experience that charcoal will not burn until energy is first supplied to it. The amount of energy, represented by the height AC, is known as the **activation energy,** which is the energy necessary to initiate the reaction between carbon and oxygen. In Fig. 85 the curves of a number of oxidation reactions reveal that the greater the activation energy required to produce reaction, the higher the kindling point of the combustible substance. The fact that construction of these potential energy curves with the help of quantum mechanics can roughly predict such properties as the kindling points of substances is one of the amazing achievements of mathematics in this twentieth century.

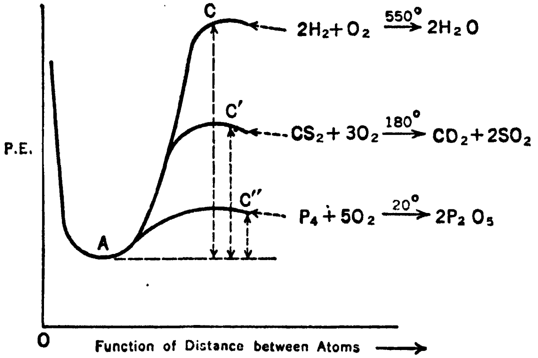

C
$2H_2+O_2 \xrightarrow{550°} 2H_2O$
C′
$CS_2+3O_2 \xrightarrow{180°} CO_2+2SO_2$
P.E.
C″
$P_4+5O_2 \xrightarrow{20°} 2P_2O_5$
A
O
Function of Distance between Atoms ⟶

FIG. 85. Energy of activation for different reactions.

An additional item in connection with activation energy is that not all the reacting molecules reach peak *C* at the same instant. That is, most reactions do not go instantaneously. Like a flock of sheep escaping over a fence, only the more active ones get over first. The rate at which the reacting molecules reach peak *C* is a measure of the speed of the chemical reaction.

What happens to the energy after the reacting substances have been raised to point C? In the case of carbon burning in oxygen, a shift of the system from point C to B releases a quantity of energy represented by the height CB (Fig. 83). Now to cause reaction, an amount of energy, given as AC, was expended; but CB energy was obtained. The total effect has been to release a quantity of energy equal to CB–AC. In the burning of carbon this amounts to 94,400 calories of heat. A reaction of this kind which results in the liberation of energy is called an **exothermic reaction.** Examples of a number of other exothermic reactions are given in Table 38.

The curve for the reaction between carbon and sulfur differs from the foregoing in that the quantity CB–AC is negative. A reaction with such a potential energy curve is said to be an **endothermic reaction.** In this case heat is consumed, not liberated, as a result of reaction. A few endothermic reactions are listed in Table 38.

**192. Forms of Energy in Chemical Reactions.**—From the foregoing paragraph it is obvious that all chemical reactions involve energy. In the discussion of these potential energy curves no restrictions were imposed with regard to the nature of that energy. That is, heat, light, mechanical motion or electricity may all play a rôle during these important chemical transformations. In fact, so many data have accumulated dealing with each of these kinds of energies that we now have separate branches of chemistry known as **thermochemistry, electrochemistry, and photochemistry.** These will now be taken up separately.

## THERMOCHEMISTRY

**193. Kinetic Nature of Heat.**—Heat is the most common form of energy accompanying chemical change. What is heat, and how is it communicated to the reacting molecules? In answering these questions, let us take as an example a molecule of oxygen. At absolute zero, there is practically complete lack of motion [1] of the molecule or of the atoms within the molecule. If this molecule is brought into contact with molecules which are in motion, some of this energy of motion is imparted to the oxygen molecule in much the same fashion as energy is transferred between two colliding billiard balls. The oxygen molecule now possesses energy, and its two atoms **vibrate.** The molecule is no longer at zero degrees, for according to the Kinetic-Molecular theory, motion is a manifestation of heat. As still more thermal energy is added, two other types of motion appear in the oxygen molecule: **rotation** of the molecule itself, and **translation** of the molecule through space. A molecule of oxygen at room temperature, for example, possesses vibrational, rotational and translational energy. In addition to this, atoms may store up potential energy in another way. We have learned that the hydrogen atom consists of a nucleus and one electron in a planetary system close to the nucleus. If exactly the correct quantities of energy are offered to the hydrogen atom, the energy is taken up and the planetary electron moves to some definite orbit further from the nucleus. We say that the **normal** hydrogen atom has become an **excited** hydrogen atom. The potential energy of the atom has been increased.

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[1] Theoretical considerations require the presence of a small *zero-point energy* even at absolute zero.

In every chemical reaction these various forms of molecular, atomic and electronic energy play a part. If the total energy content of the products is less than the total energy content of the reactants, some energy must have been dissipated to the surrounding molecules during the reaction. These neighboring molecules in taking up the energy from the reacting molecules increase their own vibrational, translational, rotational, or electronic energy content. We say that these neighboring molecules become hot; **the reaction is exothermic** (Fig. 83).

If, on the other hand, the summation of electronic, vibrational, rotational and translational energies of the products is greater than that of the reactants, some energy must have been given to the reactants by the surrounding molecules. In other words, the surrounding molecules lose some of their own energy and cool down. The reaction then is an **endothermic reaction** (Fig. 84).

**194. Exothermic and Endothermic Reactions.**—Chemical reactions involving the liberation of heat (exothermic) are more often observed and studied than those involving the consumption of heat (endothermic). Examples of each follow.

TABLE 38. SOME EXOTHERMIC AND ENDOTHERMIC REACTIONS

**Exothermic Reactions**

$C(s) + O_2 \rightarrow CO_2 + 94{,}400$ cals.

$HCl(aq.) + NaOH(aq.) \rightarrow NaCl(aq.) + H_2O(aq.) + 13{,}880$ cals.

$S + O_2 \rightarrow SO_2 + 69{,}300$ cals.

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) + 328{,}000$ cals.

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) + 136{,}828$ cals.

$Fe_2O_3 + Al \rightarrow 2Fe + Al_2O_3 + 198{,}800$ cals.

**Endothermic Reactions**

$H_2 + I_2 \rightarrow 2HI - 12{,}000$ cals.

$N_2 + O_2 \rightarrow 2NO - 43{,}000$ cals.

$C_2H_4 + H_2 \rightarrow C_2H_6 - 32{,}580$ cals.

$C + 2S \rightarrow CS_2 - 30{,}600$ cals.

The equations in Table 38 show not only the relations of the various substances concerned in a chemical reaction, but also the heat produced or consumed.

$$\underset{2 \times 2.016\text{ g.}}{2H_2} + \underset{32\text{ g.}}{O_2} \rightarrow \underset{2 \times 18.016\text{ g.}}{2H_2O} \text{ (liquid)} + 136{,}828 \text{ cal.}$$

This equation means that when 4.032 g. of hydrogen at 0° unite with 32 g. of oxygen, also at 0°, to form 36.032 g. of water at 0°, there is a sufficient quantity of heat liberated to raise the temperature of 136,828 g. of water one degree.

At one time it was postulated by Thomsen and Berthelot (1854) that the exothermicity of reaction was an indication of its probability of taking place. That is, only exothermic reactions would tend to occur. Consideration of the potential energy curves above, however, confirms the inadequacy of this hypothesis. The probability of reaction occurring is dependent upon the magnitude of the activation energy, that is, in reaching peak *C*, Fig. 83; while the heat of reaction depends also upon the shape of the curve beyond peak *C*. That there is no parallelism between the two items is shown in Table 39.

TABLE 39. ACTIVATION ENERGY AND HEAT OF REACTION

| Reaction | Activation Energy | Heat of Reaction |
|---|---|---|
| $N_2O_4 \rightarrow 2NO_2$ | 13,900 cals. | −14,600 cals. |
| $H_2 + I_2 \rightarrow 2HI$ | 40,000 " | −12,000 " |
| $N_2O \rightarrow N_2 + O$ | 53,000 " | −41,500 " |

**195. Heats of Combustion.**—The heats of reaction between oxygen and a vast number of compounds containing carbon and hydrogen, organic compounds, have been measured. Usually the combustion proceeds smoothly to carbon dioxide and water. Such thermochemical measurements yield data not only of interest concerning the fuel value of different organic materials, but information concerning the forces binding atoms together. For inasmuch as all reactions involve changes of forces between the atoms within different molecules, the heat liberated in such reactions will be an index of the magnitude of such forces. Kistiakowsky, at Harvard, has made especially accurate measurements of this nature in determining the bond forces holding atoms together in molecules. Some heats of combustion are given in the following table.

TABLE 40. HEATS OF COMBUSTION PER MOLE AT 18° C.

| | | |
|---|---|---|
| $CH_3COOH$ | Acetic acid | 209,400 cals. |
| $C_6H_6$ | Benzene | 783,400 " |
| $C_2H_5OH$ | Ethyl alcohol | 328,000 " |
| $CH_4$ | Methane | 210,800 " |
| $CH_3OH$ | Methyl alcohol | 170,900 " |
| $C_{12}H_{22}O_{11}$ | Cane sugar | 1,349,600 " |

**196. Hess' Law of Constant Heat of Reaction.**—When reactants are changed into products, the total heat evolved is the same whether the change has been achieved in one or in several steps. This is shown in the following example.

$$\underset{\text{(solid)}}{C} + \underset{\text{(gas)}}{\tfrac{1}{2}O_2} \rightarrow \underset{\text{(gas)}}{CO} + 26{,}400 \text{ cals.}$$

$$\underset{\text{(gas)}}{CO} + \underset{\text{(gas)}}{\tfrac{1}{2}O_2} \rightarrow \underset{\text{(gas)}}{CO_2} + 68{,}000 \text{ cals.}$$

$$\underset{\text{(solid)}}{C} + \underset{\text{(gas)}}{O_2} \rightarrow \underset{\text{(gas)}}{CO_2} + 94{,}400 \text{ cals.}$$

This law, which was formulated by Hess in 1840, is a corollary of the Law of Conservation of Energy. For in the above case, the heat evolved from the formation of gaseous $CO_2$ from solid C and gaseous $O_2$ will depend only upon the heat content of the initial and final states, irrespective of the path by which the reaction is affected.

Extension of Hess' Law enables us to utilize the heats of formation of substances from their elements in calculations of heats of reactions between these substances. This is illustrated in the following problem.

*Problem.*—What is the heat of reaction in the formation of aluminum oxide and iron from aluminum and iron oxide (Thermit reaction, Section 378. Heats of formation of $Al_2O_3$ and $Fe_2O_3$ from their elements are 380,000 and 198,500 calories, respectively)?

$$2Al + \tfrac{3}{2}O_2 \rightarrow Al_2O_3 + 389{,}500 \text{ cals.}$$

$$2Fe + \tfrac{3}{2}O_2 \rightarrow Fe_2O_3 + 190{,}700 \text{ cals.}$$

$$Fe_2O_3 + Al \rightarrow 2Fe + Al_2O_3 + 198{,}800 \text{ cals.} \quad \text{ANS.}$$

A number of heats of formation are given in Table 41.

TABLE 41. HEATS OF FORMATION IN CALORIES OF SOME COMPOUNDS

| | | | |
|---|---|---|---|
| $Al_2O_{3(s)}$ | 389,500 | $SO_{2(g)}$ | 69,300 |
| $Fe_2O_{3(s)}$ | 190,700 | $SO_{3(g)}$ | 91,500 |
| $NH_{3(g)}$ | 10,940 | $CO_{(g)}$ | 26,400 |
| $H_2O_{(g)}$ | 57,800 | $CO_{2(g)}$ | 94,400 |
| $H_2O_{(l)}$ | 68,400 | $CH_{4(g)}$ | 19,100 |

The generalized statement of the Law of Conservation of Energy as applied to heat energy is known as the **First Law of Thermodynamics.** It was enunciated by Helmholtz in 1847. Two other laws of thermodynamics are beyond the scope of this book. The **Second Law** has to do with two factors called free energy and entropy, and states that the entropy of a system tends towards

**a maximum. It measures the tendency of reactions to occur. The Third Law operates on a mathematical expression of the second law integrating it in such a way that it will measure the amount of reaction which should occur.**

## ELECTROCHEMISTRY

**197. Consumption and Production of Electricity.**—The *consumption* of electricity during electrolysis, electroplating and the other electrical processes taken up in support of the Arrhenius theory is ample proof that electrical energy may play a rôle in chemical reactions.

On the other hand, electricity may be *produced* by chemical reactions in a **cell,** or in a collection of cells known as an electric **battery.** When a rod of such a metal as zinc is dipped into a solution of copper sulfate, the less active metal is displaced. Thus:

$$Cu^{++} + Zn^{\circ} \rightarrow Cu^{\circ} \downarrow + Zn^{++}.$$

In terms of the electronic theory each atom of zinc gives up two electrons to the copper ion. Although there is a transfer of electrons, an electric current is not produced. In order to produce a current it is necessary to carry out the reaction in vessels which prevent the copper ion and the zinc from coming in contact. This may be accomplished by means of the apparatus illustrated in Fig. 86.

### DEMONSTRATION 68. PRODUCTION OF ELECTRICITY

Materials: Galvanometer, zinc rod, copper rod, zinc sulfate solution, copper sulfate solution, set-up in Fig. 86.

The beakers containing the solutions are connected by a so-called *salt-bridge* consisting of a glass tube filled with a solution of zinc sulfate, or other suitable electrolyte, with the ends plugged with cotton. When the rods are joined to a galvanometer by means of wire, a current of electricity may be observed. Zinc goes into solution, forming the zinc ion, $Zn^{++}$, and electrons flow through the wire and galvanometer to the copper and discharge

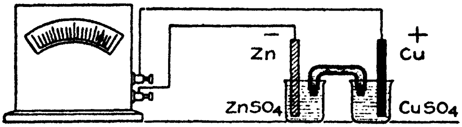


FIG. 86. Production of electrical energy.

the copper ion:

$$Zn^{\circ} - 2e \rightarrow Zn^{++}$$
$$Cu^{++} + 2e \rightarrow Cu^{\circ}.$$

Metallic copper therefore deposits on the copper rod or plate. The flow of electrons through the wire from the zinc to the copper is indicated in the figure.

In 1800, Volta produced his famous **voltaic pile** which consisted of a series of cells of alternate plates of zinc and copper each separated by a thin paper disk, and the whole moistened with dilute sulfuric acid. When the plates were joined by means of a wire a considerable difference in electrical potential was observed; electricity flowed through the wire.

### DEMONSTRATION 69. VOLTAIC CELLS

Materials: Zinc rod, dilute sulfuric acid, copper wire, galvanometer, electric door-bell, magnesium ribbon, battery set, 100 cc. beaker, 400 cc. beaker.

When a copper wire and zinc rod are immersed in sulfuric acid and connected with the galvanometer, a current of electricity is produced. That is, some of the heat of reaction is transformed into electrical energy. In a similar way, enough electricity will be generated to ring an electric door-bell when it is connected to a copper wire and magnesium ribbon and the two are immersed in dilute sulfuric acid.

In the above experiments the metal loses two electrons upon going into solution. These electrons pass through the copper wire to the hydrogen ions, and hydrogen gas is produced at the cathode. The voltaic cell therefore provides a wire through which the electrons can flow to reach the hydrogen ions.

$$Zn^{\circ} + 2H^{+} \rightarrow Zn^{++} + H_2\uparrow.$$
$$Mg^{\circ} + 2H^{+} \rightarrow Mg^{++} + H_2\uparrow.$$

**198. Dry Cells.**—Dry cells produced on a large scale for bells, flashlights, telephones, radios, etc., are not truly *dry;* for if the contents of the cell were really dry, it would not function.

Instead of containing a fluid, the cells contain a moist mixture in the form of a paste, and can therefore be transported more conveniently than can those containing liquids. A section of a very common dry cell is shown in Fig. 87. A carbon rod constitutes the positive electrode, and it is packed in a mixture of manganese dioxide, graphite and crushed charcoal, moistened with a solution of ammonium chloride, often mixed with zinc chloride. A zinc can serves as the negative electrode, the can being separated from the manganese dioxide mixture by absorbent paper, pulpboard, or a muslin bag. Sawdust or sand is placed above the manganese dioxide mixture, and the top of the apparatus is sealed with wax or pitch.

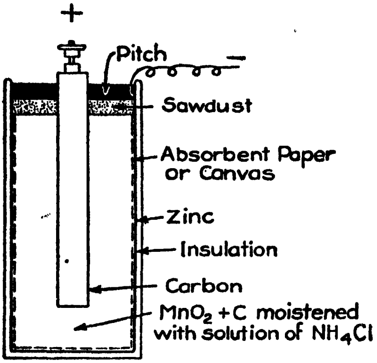

+
Pitch
−
Sawdust
Absorbent Paper or Canvas
Zinc
Insulation
Carbon
$MnO_2$ + C moistened with solution of $NH_4Cl$

FIG. 87. A dry cell.

As with wet cells, during operation the zinc forms ions at the negative electrode, while hydrogen is formed at the positive electrode. However, the manganese dioxide oxidizes the hydrogen to water, so that little hydrogen is liberated at the positive (carbon) electrode. As the reaction proceeds:

$$Zn + 2NH_4Cl \rightarrow ZnCl_2, 2NH_3 + H_2 + \text{energy},$$

hydrogen tends to collect around the carbon electrode, and reduce the voltage; but upon standing, the cell regains its voltage as the hydrogen is oxidized to water:

$$2MnO_2 + H_2 \rightarrow Mn_2O_3 + H_2O.$$

Such a cell when fresh has a voltage of 1.54 V.

The **Cadmium** or **Weston Standard Cell** is employed for measuring E.M.F.; it gives a constant value of 1.0183 volts at 20°. It contains

$$Hg/Hg_2SO_4 \text{ (sat. soln.) :: } CaSO_4 \text{ (sat. soln.)}/Cd\text{-}Hg$$

in an H-shaped cell. The limb containing the cadmium amalgam is the cathode.

**199. The Lead Storage Battery.**—In the construction of a **storage cell,** or **lead accumulator,** plates of leaden gratings are prepared, and one of the plates is filled with spongy lead and the other with lead dioxide, $PbO_2$, paste. Pairs of these plates are placed in a cell and dilute sulfuric acid (sp. gr. about 1.2) added. When the plates are connected by means of a wire, a current with an electromotive force of about 2 volts is produced as the cell is discharged. The reactions which occur in a storage battery are illustrated in the following diagram.

$$\begin{tikzcd}
- \text{ pole} & & + \text{ pole} & \\
Pb \arrow[d, shift left, "\text{discharging}"] & H_2SO_4 \arrow[d, shift left, "\text{discharging}"] & PbO_2 \arrow[d, shift left, "\text{discharging}"] & \text{(Battery fully charged)} \\
PbSO_4 \arrow[u, shift left, "\text{charging}"] & H_2O \arrow[u, shift left, "\text{charging}"] & PbSO_4 \arrow[u, shift left, "\text{charging}"] & \text{(Battery fully discharged)}
\end{tikzcd}$$

During the discharging of the battery, the lead at the negative pole is losing two electrons, while the lead dioxide at the positive pole is gaining two electrons. Both substances are transformed into lead sulfate. Sulfuric acid, specific gravity 1.84, is replaced by water, specific gravity 1.0. For this reason the determination of the specific gravity of the solution in a storage battery indicates how far the battery is discharged. A fully charged battery contains approximately 40% $H_2SO_4$ by weight, while a battery which has discharged considerably may contain as little as 15% sulfuric acid. For this reason the density of the sulfuric acid drops from 1.3 to 1.1 during discharging.

The reaction which is occurring during the discharging is as follows:

$$PbO_2 + Pb + 2H_2SO_4 \xrightarrow{\text{(discharging)}} 2PbSO_4 + 2H_2O.$$

After the battery is discharged, it is recharged by passing through it a current from a dynamo in the direction opposite from that produced by the battery. The processes are reversed; lead sulfate is transformed into lead at the negative pole and into lead dioxide at the positive pole, electrons being lost from the positive and added to the negative pole. The equation for the act of charging is, of course, the reverse of the equation given above for the act of discharging.

In the **Edison storage cell**, the active material of the positive plate is an oxide or oxides of nickel, while that of the negative pole is iron. The electrolyte is a 21 per cent solution of potassium hydroxide with a small amount of lithium hydroxide. When the cell discharges and is recharged the reversible action may be shown by the following equation:

$$Ni_2O_3 + Fe + 3H_2O \rightleftarrows 2Ni(OH)_2 + Fe(OH)_2.$$

$$\text{Discharge} \rightarrow \leftarrow \text{Charge}$$

**200. Oxidation-Reduction Reactions.**—It will be recalled (59) that when a substance is oxidized it loses electrons, while a substance which is reduced gains electrons. Thus, when a solution of ferrous chloride is treated with chlorine, $Fe^{++}$ is oxidized, while the chlorine is reduced. The electrons lost by the ferrous ions are passed over to the chlorine atoms to form chloride ions:

$$2Fe^{++} + Cl_2^0 \rightarrow 2Fe^{+++} + 2Cl^-.$$

Chlorine is therefore the oxidizing agent and ferrous ions the reducing agent. This may be regarded as a typical oxidation-reduction reaction. From this reaction we see that **electricity may be produced by an oxidation-reduction reaction.**

### DEMONSTRATION 70. ELECTRICITY FROM AN OXIDATION-REDUCTION[1] REACTION

Materials: Set-up in Fig. 88.

**The salt-bridge contains ferric chloride. A small quantity of ferric chloride is also added to the beaker containing the chlorine water to make it a conductor.**

The electrons flow from the ferrous chloride beaker through the galvanometer to the solution of chlorine water where chlorine molecules are reduced to chloride ions. In the other beaker, ferric chloride is formed.

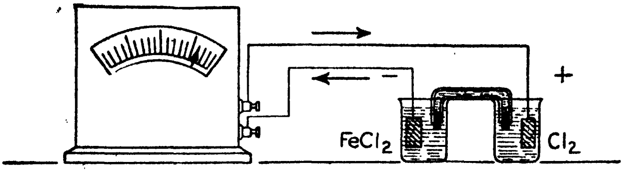


FIG. 88. Chemical reaction producing electricity (Dem. 70).

Just as an electric current can be *produced* as the result of an oxidation-reduction reaction, so the converse may be achieved; *i.e.*, electrical energy can be *consumed* in bringing about an oxidation-reduction reaction.

### DEMONSTRATION 71. AN OXIDATION-REDUCTION REACTION CAUSED BY ELECTRICITY

Materials: Two dry cells, two 400-cc. beakers, ferric chloride solution, dilute hydrochloric acid. Set-up essentially that of Fig. 88 where the galvanometer is replaced by two dry cells. One beaker contains ferric chloride, the other contains hydrochloric acid, and the salt-bridge contains ferric chloride.

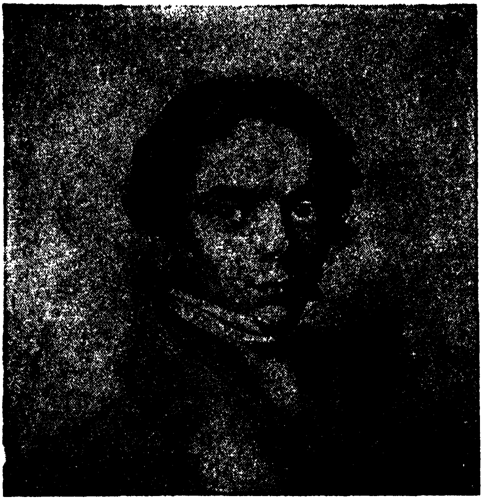
When an electric current is passed through the solution, the chloride ions lose electrons and appear as free chlorine bubbles; the electrons flow through the wire around to the ferric chloride where the ferric ion is reduced to ferrous ion.

Other oxidation-reduction reactions may similarly be arranged to yield or to consume an electric current.

## PHOTOCHEMISTRY

**201. Light Producing Chemical Change.**—Light energy, too, may be consumed or evolved during a chemical change. Although light is ordinarily thought of as a kind of wave motion, it also consists of particles called **photons** or **quanta.** A 40-watt lamp bulb emits about $10^{20}$ quanta per second.

How is light absorbed by a reacting molecule? To answer this we must turn to a rough picture of the atom. It consists of a central sun about which planetary electrons are moving in definite orbits. The **normal atom** has electrons moving in orbits relatively close to the nucleus; but there are, in addition, other orbits considerably further out to which the planetary electrons may jump, forming **excited atoms.** To pull the electrons to an outer orbit, a definite quantity of energy must be supplied to the atom. The so-called **energy levels** tell us how much energy must

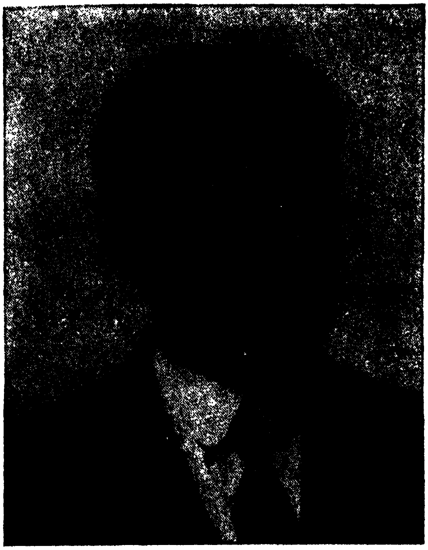


**Michael Faraday** (1791–1867)

Son of a Surrey blacksmith, apprenticed to a bookbinder at the age of fourteen, without opportunity to receive systematic instruction, he became Davy's assistant, and later succeeded him at the Royal Institution in 1825. Faraday discovered the induced current which is the basis of our electrical civilization; also, the laws of electrolysis, and benzene. He liquefied several gases.

**Irving Langmuir** (1881–     )

Born at Brooklyn, N. Y.; educated at the Columbia School of Mines and in Germany; a research director of the General Electric Company at Schenectady, N. Y., Langmuir received the Nobel Prize Award in Chemistry in 1934 for his work on tungsten-lamp filaments, mercury high-vacuum pumps, atomic hydrogen, atomic structure, mono-molecular layers, and so forth. He was President of the American Chemical Society in 1929.



be supplied to raise the electrons to various excited states. Now if an atom is radiated with light quanta whose energy corresponds to the additional energy of one of these upper levels, a quantum is absorbed by the normal atom changing it into an excited atom. By this same mechanism a normal *molecule* can absorb a light quantum and move into an excited state, which may include definite (quantized) energy levels of vibration and rotation as well as electronic energy states.

If, then, we shine light upon a material and a chemical reaction occurs, we may picture the reacting molecules as absorbing quanta of light, thereby becoming excited. This absorbed energy is sufficient to raise them over the potential energy hump (**191**) necessary before reaction can occur.

### DEMONSTRATION 72. PHOTOCHEMICAL DECOMPOSITION OF AgCl

Materials: Solutions of silver nitrate and sodium chloride, funnel and filter paper, 400 cc. beaker, magnesium ribbon, burner, forceps.

When silver chloride is freshly precipitated it is pure white. If half of the precipitate is exposed to the light of a burning magnesium ribbon, the other half being shielded, the exposed half turns dark purple. In terms of the photochemical mechanism pictured above, the silver chloride molecules have absorbed light quanta, and this furnishes enough energy to the AgCl molecules to decompose them into metallic Ag and gaseous $Cl_2$. It is the principle involved in photography. The sensitive photographic film contains an emulsion of gelatin and silver bromide and silver chloride, which undergo the photochemical changes described for the demonstration above.

The quanta of any given color of light all have the same energy content. As we traverse the spectrum from infra-red to red to yellow to green to blue to violet to ultraviolet, we pass to quanta of larger energies. Ultraviolet light of a wave length of 3000 Ångstrom units (1 Å = $10^{-8}$ centimeters) has energy quanta of approximately 4.6 volts or 100,000 calories. Yellow light of a wave length of 6000 Å has quanta with energy only half as great, 2.3 volts, or 50,000 calories. Since many chemical reactions require activation energies (**191**) of the order of 100,000 calories, we find that the visible spectrum does not cause a great many chemical reactions. On the other hand, the ultraviolet light furnishing 100,000 calorie quanta will be photochemically active. For this reason we sunburn from the ultraviolet not the visible rays of the sun. For the same reason Vita-glass or other special glasses transparent to ultraviolet will be of therapeutic value, whereas ordinary window glass which will not transmit light of wave lengths shorter than about 3200 Å will be useless in passing rays which stimulate healthy chemical reactions in the skin.

In all of these cases, the mechanism of the photochemical process is that of light quanta being absorbed, and thereby raising the molecules over the potential energy hump so that reaction will occur.

**202. Chemical Reactions Producing Light.**—A chemical reaction may *evolve* light.

### DEMONSTRATION 73. EVOLUTION OF LIGHT DURING REACTION

Materials: Magnesium ribbon, phosphorus, forceps, deflagrating spoon, 400 cc. beaker, 250 cc. Erlenmeyer flask, U-tube, large test-tube, (a) 1 g. luminol (3-amino-phthal-hydrazid, Eastman Kodak Co.) plus 100 cc. of 5 per cent $NaOH$; (b) 2.5 g. potassium ferricyanide plus 100 cc. of 3 per cent $H_2O_2$; jar containing 15 liters of water; towel.

Burning magnesium ribbon or phosphorus produces intense light and heat. Pouring ingredients (a) and (b) into the jar of water affects an organic oxidation reaction which gives off "cold" light. In a darkened room this glowing liquid may be clearly distinguished as it is poured into containers of various shapes. The mechanism of this liberation of light is the converse of light absorption. During chemical reaction the energy of reaction produces excited molecules. These excited molecules return spontaneously to their normal state, and, in so doing, the energy of excitation is emitted solely as visible light.

**203. Bioluminescence.**—At least forty orders of animals and two groups of plants are able to produce *cold light*, without the accompaniment of heat.

The luminescence of damp wood (*fox-fire*) is due to a fungus in the wood; and it is well known that dead fish or meat may glow in the dark, due to bacteria. Some small creatures of the sea *phosphoresce* when stimulated by the churn of a boat's propeller; but the glow has nothing to do with the element phosphorus.

Robert Boyle (1667) showed that a small piece of luminescent wood ceases to glow when air is removed: luminescence therefore requires the presence of oxygen.

The higher forms of animal life, such as the firefly, are able to produce light without external stimulation. The light is the result of chemical oxidation of a simple protein, **luciferin**, the heat of reaction appearing as light, *i.e.*,

$$\underset{\text{luciferin}}{LH_2} + \underset{\text{oxygen}}{\tfrac{1}{2}O_2} \rightleftarrows \underset{\text{oxy-luciferin}}{L} + \underset{\text{water}}{H_2O} + \text{light}.$$

The reaction is reversible, and between flashes the firefly is busy regenerating luciferin from oxy-luciferin. As is evident from the equation, both water and oxygen are necessary for the processes to occur.

E. N. Harvey has made an extensive study of this reaction. The oxidation of the luciferin is hastened by the presence of an enzyme, **luciferase**, in the bioluminescent body.

We have already referred to the glow as *cold light*. This indicates that little heat is generated. Man has something to learn from this >90% efficient process of the firefly; for even the most modern luminescent tubes are only 15% efficient, while the tungsten filament bulb dissipates as heat instead of light nearly 95% of the electricity it consumes. Perhaps someday *cold light* will become an industrial reality.

**204. The Einstein Photochemical Equivalence Law.**—In 1906 young Albert Einstein published five fundamental papers in five independent fields. One of them had to do with photochemical processes. Einstein showed how to calculate the number of quanta in a beam of light, and postulated that for each quantum absorbed one molecule should react.

The chemists immediately focused their attention upon this postulate, and verified it experimentally for a number of reactions, some of which are listed in Table 42. They established the **Einstein Photochemical Equivalence Law.**

TABLE 42. QUANTUM YIELDS FOR VARIOUS REACTIONS

| Reaction | Wavelength | Quantum Yield |
|---|---|---|
| $COBr_2 \rightarrow CO + Br_2$ | <3200Å | 1 |
| $SO_2 + Cl_2 \rightarrow SO_2Cl_2$ | 4200 | ~1 |
| $HI \rightarrow \frac{1}{2}H_2 + \frac{1}{2}I_2$ | 2070–2820 | 1 |
| $NOCl \rightarrow NO + \frac{1}{2}Cl_2$ | 3650–6300 | 1 |
| $2Fe^{++} + I_2 \rightarrow 2Fe^{+++} + 2I^-$ | 4000–4200 | 1 |
| $H_2 + Cl_2 \rightarrow 2HCl$ | visible | >1,000,000 |
| $Na_2SO_3 + \frac{1}{2}O_2 \rightarrow Na_2SO_4$ | 3660 | 50,000 |

The law is in agreement with our foregoing description of the mechanism of photochemical processes. For *one* quantum should produce *one* excited molecule, which in turn should react to give a definite number of product molecules. The heat of reaction is assumed to be redistributed throughout all of the molecules in the system (equipartition of energy).

**205. Chain Reactions.**—In 1912 Nernst, in Berlin, found that the combination of hydrogen with chlorine did not obey the Einstein Law (Table 42). More than a million molecules of hydrogen chloride were formed for each quantum of light absorbed. Such a reaction was called a **chain reaction.**

### DEMONSTRATION 74. HCl CHAIN REACTION

Materials: Magnesium ribbon, forceps, glove, sources of hydrogen and chlorine; large test-tube, filled completely with water, clamped over a trough of water so that *only the lip of the tube* is under the water; row of dominoes fastened to a board with adhesive tape (Fig. 89).

**Care.**—*When a burning magnesium ribbon is brought into proximity with the tube filled half with hydrogen, half with chlorine, a violent photochemical explosion takes place.* The two gases must be extremely pure, a single bubble of air completely inhibiting the explosion.

Nernst assumed that the primary process in the hydrogen chlorine reaction obeys the Einstein Law. The chlorine is the species which absorbs the light.

$Cl_2$ + 1 quantum of light → Cl + Cl (primary photochemical process).

This primary step, however, is succeeded by a sequence of steps. This was called **a chain reaction.**

$$\left.\begin{array}{l} \left.\begin{array}{l} Cl + H_2 \rightarrow HCl + H \\ H + Cl_2 \rightarrow HCl + Cl \end{array}\right\}\text{link No. 1} \\ \hdashline \left.\begin{array}{l} Cl + H_2 \rightarrow HCl + H \\ H + Cl_2 \rightarrow HCl + Cl \end{array}\right\}\text{link No. 2} \\ \hdashline Cl + H_2 \rightarrow \text{etc.}\cdots \quad \text{etc.}\cdots \end{array}\right\}\text{chain reaction}$$

Thus from a single chlorine atom an infinite number of HCl molecules form, but for the probability that the chain might be broken by any reaction which destroys chain carriers, such as

$$\left.\begin{array}{r} Cl + Cl \rightarrow Cl_2 \\ H + Cl \rightarrow HCl \\ H + \text{impurities} \rightarrow HX \\ Cl + \text{impurities} \rightarrow YCl \end{array}\right\}\begin{array}{l}\text{chain breaking} \\ \text{steps}\end{array}$$

The mechanism of chain reactions may be demonstrated with the domino board. Reaction is represented by a falling domino. One quantum, one impulse, will knock over a whole row of dominoes.

Subsequently a large number of chain reactions were discovered. Invariably these reactions were sensitive to poisoning, the poisons or **inhibitors** acting by breaking the chains before many chain links could be completed. This may be illustrated on the domino board by inserting a pencil in the path of the falling dominoes: one inhibitor molecule (the pencil) can prevent the reaction of a large number of molecules (falling dominoes).

By 1923 Christiansen, in Copenhagen, postulated that chain reactions could be initiated by heat as well as by light. In support of this theory it was pointed out by Bäckström that several oxidation reactions were sensitive to the same inhibitors and to the same degree whether the reaction were initiated by light or by heat; that is, that reaction chains were set up in either case.

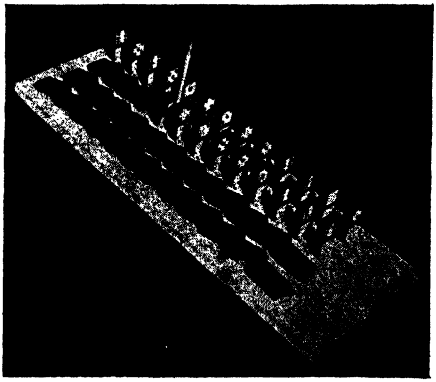


FIG. 89. Demonstrating a chain reaction. The pencil is an "inhibitor" which has broken a chain.

A wave of research followed this new concept of reaction mechanism, and between the years 1928–1940 there were over 30,000 separate research papers published on chain reactions alone.

The explosion of hydrogen and oxygen is an interesting thermal chain reaction. While the student normally writes the equation

$$2H_2 + O_2 \rightarrow 2H_2O,$$

this represents only the initial reactants and the final products. The mechanism of reaction is certainly not a collision of 2 hydrogen molecules with 1 oxygen molecule and the emergence of 2 water molecules from the collision. Actually, the mechanism depends upon the temperature and pressure at which the explosion is carried out. At 500° C. and 50 mm. there is a chain reaction initiated by hydrogen atoms liberated from the walls of the containing vessel:

$$\left.\begin{array}{l} H + H_2 + O_2 \rightarrow H_2O + OH \\ OH + H_2 \rightarrow H_2O + H. \end{array}\right\}\text{chain reaction}$$

From this the student learns that the simplest reactions may have very complicated reaction mechanisms indeed.

### MECHANICAL ENERGY

**206. Mechanical Energy Produced or Consumed.**—In exploding hydrogen and oxygen, or dynamite, or dust (Demonstration 18, section 41) the energy of reaction appears largely as mechanical energy of sound or motion.

DEMONSTRATION 75. CHEMICAL REACTION AND MECHANICAL ENERGY

Materials: Mortar, pestle, solid silver chloride, mercuric nitrate, potassium iodide, bottle of hydrogen and oxygen in a protecting wire cage and towel.

Vice versa, chemical reaction can be produced by mechanical energy. Thus when solid mercuric nitrate is rubbed with solid potassium iodide, chemical reaction occurs. Also, vigorously grinding silver chloride consumes mechanical energy and liberates metallic silver and gaseous chlorine. The explosion of hydrogen and oxygen gives forth a thunderous sound, the result of compression waves in the air.

GENERAL CONCLUSIONS: **A chemical reaction is always accompanied by the absorption or liberation of energy. This energy may be in various forms, *e.g.*, heat, electricity, light or mechanical energy.**

## QUESTION REVIEW

**Transformations of energy (189).**

I. POTENTIAL ENERGY CURVES. **Of molecules (190). Of reactions (191).**

1. Draw a diagram showing the forces involved when two electrons are brought together. Contrast with the case of two hydrogen atoms being brought together. Of two neon atoms brought together. Label coordinates.
2. Draw a potential energy curve for an exothermic reaction. For an endothermic reaction. Indicate energy of activation and heat of reaction on the curves.

**Forms of energy in chemical reactions (192).**

II. THERMOCHEMISTRY. **Heat (193). Exothermic and endothermic reactions (194). Heat of combustion (195). Hess' law (196).**

3. What is the difference between a normal and an excited hydrogen atom? Sketch them.
4. Criticize the postulate that the exothermicity of reaction is an indication of the probability of its taking place.
5. What are heats of combustion? How are they measured? Of what interest are they in addition to telling us the fuel value of different organic materials?
6. Neglecting cost, which has a greater fuel value: a ton of sucrose or a ton of charcoal?
7. Calculate the heat of formation of a mole of each of the following substances: water vapor, carbon dioxide, sulfur dioxide, copper oxide, magnesium oxide. (See Appendix.)
8. From data in the table on heats of formation calculate the heat of reaction between $SO_2$ and $O_2$ to give $SO_3$.

III. ELECTROCHEMISTRY (197). **Dry cells (198). Storage battery (199). Oxidation-reduction (200).**

9. Describe an experiment illustrating the production and the consumption of electricity during chemical reaction.
10. Write an equation showing the production of electricity in the dry cell. Also, an equation illustrating how the formation of hydrogen at the positive electrode is prevented.
11. Write an equation illustrating the discharging of the storage battery. Illustrating the charging of a storage battery.

12. **Describe experiments demonstrating the production and the consumption of electricity from oxidation-reduction reactions.**

IV. PHOTOCHEMISTRY. **Light consumed or produced (201–202). Bioluminescence (203). Einstein's law (204). Chain reactions (205).**

13. Define and illustrate: photons, quanta, normal atom, excited atom, energy levels, potential energy hump.
14. Describe how light is absorbed by a molecule which undergoes chemical reaction.
15. ✓ In terms of energy of activation why is it that we do not sunburn behind windows of ordinary window glass?
16. Discuss the evolution of light during chemical reaction in terms of normal and excited molecules.
17. Does phosphorescence have anything to do with phosphorus? Does it have anything to do with oxygen? with water? with luciferin and luciferase?
18. What has Einstein contributed to the field of photochemistry? Explain the law in terms of a reaction mechanism. What is meant by *equipartition of energy*?
19. Write equations showing chain mechanisms for the combination of hydrogen and chlorine, and for the combination of hydrogen and oxygen. How may these chains be broken?

V. MECHANICAL ENERGY (206).

**Reading References:** Articles number 8, 9, 52, 75, 321, 334 and 423 in the Appendix.

# CHAPTER XVII

# EQUILIBRIUM

## RATE OF REACTION

**207. The Speed of Chemical Change.**—In section 191 we saw that a molecule would not undergo chemical reaction until sufficient activation energy had been imparted to it. Also, that not all molecules attained this state simultaneously; otherwise every chemical reaction would be virtually explosive.

### DEMONSTRATION 76. THE IODINE CLOCK

Materials: Stop watch, two 100-cc. graduates, two 400-cc. beakers, two solutions as follows. (1) 2 g. potassium iodate, $KIO_3$, in a liter of water. (2) 0.4 g. of sodium bisulfite ($NaHSO_3$), 5 cc. 1 M $H_2SO_4$, and 2 g. soluble starch in a liter of water. It may be necessary separately to dissolve the starch in boiling water; if so, cool before adding the other chemicals. The solutions may be kept from year to year; (2) may be revived with a little sulfuric acid.

Solution (1) is essentially iodic acid, $HIO_3$, which is formed by the interaction of $KIO_3$ and $H_2SO_4$. Solution (2) is essentially sulfurous acid, $H_2SO_3$. Upon mixing equal volumes of the two solutions, no reaction apparently takes place. However, after an exact number of seconds, which may be checked with a stop watch, the solution suddenly becomes blue.

The explanation of this experiment is based upon *consecutive reactions:*

$$\begin{array}{lll} HIO_3 + 3H_2SO_3 & \rightarrow HI + 3H_2SO_4 & (1), \text{(slow)} \\ HIO_3 + 5HI & \rightarrow 3I_2 + 3H_2O & (2), \text{(fast)} \\ I_2 + H_2SO_3 + H_2O & \rightarrow H_2SO_4 + 2HI & (3). \text{(fastest)} \end{array}$$

The solutions are so prepared that $HIO_3$ is present in excess. Reaction (1) is not so rapid as reaction (2), but reaction (3) is very much faster. The result is that so long as $H_2SO_3$ is present, iodine cannot be detected, because it is used up in reaction (3) as quickly as it is formed. As soon, however, as all the $H_2SO_3$ is consumed, reaction (3) necessarily stops, and the iodine set free in reaction (2), which keeps on going, instantly colors the starch.

**208. Factors Influencing Rate of Reaction.**—The hump of the potential energy curves for the foregoing three reactions is highest for reaction 1 and lowest for reaction 3. Rate of reaction is essentially a measurement of the rate at which the reactive molecules can get to the peak of the hump, *i.e.*, can acquire sufficient energy of activation to carry them over the hump (**191**). Some of these factors will be briefly considered.

Obviously, **concentration of the reacting species** determines rate of reaction. If the concentration is greater, more molecules reach the peak of the potential energy curve during a given interval of time. In the iodine clock experiment, the use of more $HIO_3$ increases the rate at which the $H_2SO_3$ is consumed, thereby shortening the time before the solution flashes blue-black. To take another example, an iron nail does not burn as rapidly as iron filings because the quantity of iron exposed to the air is vastly greater in the case of the filings. This effect of concentration was formulated as the very important **Principle of Mass Action** by Guldberg and Waage in 1867, which stated that **the speed of chemical reaction is proportional to the "active mass" of each of the reacting substances.** In the foregoing case of burning iron, the rate of reaction is determined by the ratio of the reacting species, oxygen to iron surface, rather than by the total quantity of iron present. The term *concentration*, then, is restricted to the *material actually available for reaction.* In this same sense, hydrogen is not liberated more rapidly by treating a small piece of zinc with a large quantity of dilute sulfuric acid than it is by using a smaller quantity; but 10 cc. of 5 *N* acid will interact more rapidly with a given mass of zinc than will 10 cc. of a more dilute acid, say, 2 *N*. In the case of the more concentrated acid, a larger number of molecules of sulfuric acid come into contact with the zinc in a unit of time.

For gaseous reactions, increased **pressure** will increase the number of moles reacting per minute. In this case we are increasing the total number of molecules which may possess sufficient energy of activation to take them over the potential energy hump. This is why most elements burn more vigorously in pure oxygen than in air; for the pressure of oxygen in the air is only one-fifth of an atmosphere.

**Temperature** likewise influences rate of reaction. For most reactions an increase of 10° C. approximately doubles the rate of reaction. Thus a reaction which at 20° C. proceeds at a given rate usually goes twice as fast at 30° C., 4 times faster at 40° C., and 8 times faster at 50° C. For this same reason the Birdseye frosted foods at the temperature of dry ice, approximately 110° below room temperature, will spoil $2^{110/10} = 2048$ times more slowly than they do at room temperature. This means that in

1 year the frosted food at −78° C. would spoil about as much as food at 28° C. would spoil in 3 hours. The relative distribution of energy among molecules in a system may be represented by a curve formulated by Clark Maxwell in 1882, and shown in Fig. 90. Only those molecules having an energy content in excess of C contain sufficient energy of activation to raise them over the potential energy hump, *i.e.*, to cause them to react. The number of such molecules is represented by the shaded area in the figure. That is, AC on this curve corresponds to AC in figures 83 and 84. An increase in temperature of 10° displaces the curve slightly to the right; and it will be observed that although this is but a small displacement along the abscissa, it has doubled the area of the curve beyond the threshold value C. In terms of rate of reaction, the number of molecules raised over the potential hump is doubled by a 10° rise.

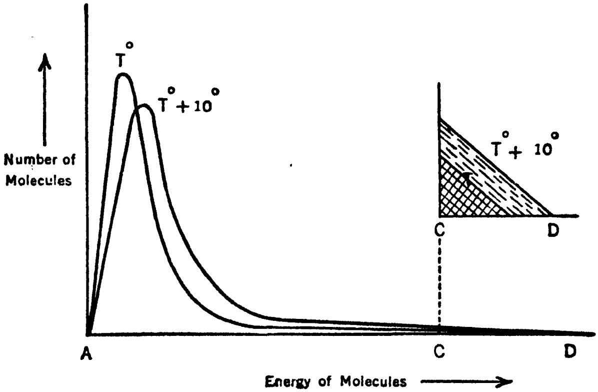


FIG. 90. Maxwell-Boltzmann energy-distribution curves. Only molecules with energies greater than C react. *Insert:* portion CD increased more than a billion-fold. The two shaded triangles are at T° and T° + 10° respectively. Note that a 10° rise may double the area beyond C (*i.e.*, may double the number of reacting molecules).

### DEMONSTRATION 77. TEMPERATURE COEFFICIENT

Materials: Iodine clock solutions as in Demonstration 76. Cake of ice, burner, tripod, wire gauze, three 400-cc. beakers.

The influence of temperature upon rate of reaction may be demonstrated by carrying out the iodine clock reaction simultaneously in three separate beakers, one on a cake of ice, another at room temperature, and the third at about 60° (not boiling).

The beaker kept on ice takes many times longer than the warm beaker before it flashes blue-black.

### CHEMICAL EQUILIBRIUM

**209. Reversible Reactions.**—Many reactions may proceed in either direction. Thus mercuric oxide decomposes into mercury and oxygen upon heating, whereas under other conditions mercury and oxygen recombine to form mercuric oxide:

$$2HgO \underset{200^\circ}{\overset{400^\circ}{\rightleftarrows}} 2Hg + O_2.$$

This is called a **reversible reaction.** At one temperature decomposition is favored; at a somewhat lower temperature combination predominates.

Again, when hydrogen is passed over hot magnetic oxide of iron, the oxide is reduced to metallic iron; also, hydrogen can be formed by reducing steam with hot iron:

$$\text{(left)} \qquad Fe_3O_4 + 4H_2 \rightleftarrows 3Fe + 4H_2O. \qquad \text{(right)}$$

If iron oxide and hydrogen are heated together in a closed vessel, say at 440°, a chemical equilibrium is (See Fig. 20) between the substances on the left of the equation and those on the right. This condition of apparent rest or equilibrium is reached when the speed of the action to the right is just balanced by the speed of the action in the reverse direction. Equilibrium also would be established by starting with the pair of substances—iron and steam. If we start by heating iron oxide and hydrogen together, the speed of the forward action begins at a maximum, while the speed of the reverse action starts at zero. The speed of the forward action becomes slower and slower, and that of the reverse action faster and faster until the two speeds are equal. **At equilibrium there is no further change in the concentrations of the reacting substances.** It should be borne in mind, however, that we have not a state of repose, but a balanced action.

Experiment shows that at 440° equilibrium is established when the volume of the steam is to the volume of hydrogen nearly as 6 : 1. This means that if 6 volumes of steam and 1 volume of hydrogen are passed over iron oxide or iron at 440°, no apparent change will take place; for the gaseous mixture will have the same composition after passing through the tube as it had upon entering it.

Other common reversible actions are as follows:

$$\begin{array}{ll} PCl_5 & \rightleftarrows PCl_3 + Cl_2, \\ 4HCl + O_2 & \rightleftarrows 2H_2O + 2Cl_2, \\ 2HI & \rightleftarrows H_2 + I_2, \\ NaCl + H_2SO_4 & \rightleftarrows NaHSO_4 + HCl. \end{array}$$

**210. Law of Mobile Equilibrium.**—To the industrialist seeking to obtain a maximum yield of a certain product, it is vital to ascertain those conditions, such as temperature and pressure, which shift the equilibrium to the profitable side of the equation.

**LeChatelier** has formulated a law which can be applied in predicting the effect of concentration, pressure, heat and other forms of energy. The law states that **if a force** (concentration, pressure, heat) **is brought to bear upon a system in equilibrium, the equilibrium shifts to a new value, and** a chemical reaction occurs predominately **in that direction which tends to diminish the effect of the applied force.** We shall discuss these forces in the light of LeChatelier's law.

**211. Concentration Shifting Equilibrium.**—The effect of adding reactants or products to a system in chemical equilibrium may be illustrated by a reaction studied by J. H. Gladstone in 1855.

### DEMONSTRATION 78. CONCENTRATION SHIFTING $Fe(CNS)_3$ EQUILIBRIUM

Materials: Four beakers, four stirring rods; solid ferric chloride, ammonium thiocyanate, and ammonium chloride; concentrated solutions of these three substances; a solution containing 20 cc. N/10 $FeCl_3$ plus 20 cc. N/10 $NH_4CNS$ plus 2000 cc. water.

When a very dilute solution of ferric chloride, $FeCl_3$, is treated with a dilute solution of ammonium thiocyanate, $NH_4CNS$, a blood-red solution is obtained, due to the formation of ferric thiocyanate, $Fe(CNS)_3$. The reaction is reversible:

$$\text{(left)} \quad \underset{\text{reddish}}{FeCl_3} + \underset{\text{colorless}}{3NH_4CNS} \rightleftarrows \underset{\text{deep red}}{\mathbf{Fe(CNS)_3}} + \underset{\text{colorless}}{3NH_4Cl} \quad \text{(right)}$$

The solution is distributed to the four beakers. When ferric chloride, either solid or in solution, is added to one of the beakers the color deepens; this indicates that a change to the right is favored, increasing the concentration of deep red ferric thiocyanate. Likewise when ammonium thiocyanate is added to the second beaker, the color deepens on account of the formation of more ferric thiocyanate. On the other hand, upon addition of ammonium chloride to the third beaker the reddish color partially fades; the equilibrium is shifted to the left. This shows that when the concentration of ammonium chloride is increased, the molecules of the substances on the right-hand side of the equation encounter each other more frequently in a given period of time; consequently they interact to form more of the substances on the left.

At equilibrium, all four compounds exist in solution, and their concentrations are definite. In terms of LeChatelier's law, an attempt to increase the concentration of any particular substance by adding more of that substance causes a chemical reaction so as to use up the added substance; the equilibrium shifts and forms more of the substances on the other side of the equation.

**212. Principle of Mass Action.**—In 1864–79 Guldberg and Waage investigated the effect of concentration upon the rates of both the forward and the back reactions. They also formulated a relationship which exists between the concentrations of the reactants and of the products, at equilibrium.[1] For the general reaction

$$aA + bB \cdots \rightleftarrows cC + dD \cdots \text{ etc.}$$

their formulation of the concentration relationships was as follows:

$$\frac{(\text{conc.}_C)^c \times (\text{conc.}_D)^d}{(\text{conc.}_A)^a \times (\text{conc.}_B)^b} = K.$$

**K is called the equilibrium constant.** Notice that it is customary to place the *products* in the numerator and the *reactants* in the denominator.

The above formulation signifies that at any fixed temperature there is a definite mathematical relationship between the concentrations of the various reacting species in a reversible reaction.

**213. Concentration and the Equilibrium Constant.**—The following problem will serve to clarify the significance and usefulness of the equilibrium expression in chemical calculations.

*Problem.*—A certain reaction is found to be reversible. At a given temperature the following relative quantities are present at equilibrium:

$$\underset{\text{1 mole}}{A} \rightleftarrows \underset{\text{2 moles}}{B} + \underset{\text{2 moles}}{C}$$

If 1 additional mole of $C$ is added to this equilibrium mixture, what will the new concentration of the substance be?

---

[1] NOTE TO THE TEACHER: this text purposely omits the kinetic derivation of the so-called Law of Mass Action, inasmuch as few reactions have rates corresponding to their stoichiometric equations. A kinetic derivation would therefore seldom apply. Guldberg and Waage realized this in their original papers. See FROST: *J. Chem. Educ.* **18**, 272 (1941).

*Answer.*—If 1 mole of $C$ is added (new $\text{conc.}_C = 3$) a reaction will occur, which according to LeChatelier's law will counteract the addition by reducing the concentration of $C$ to less than 3.

Let $x$ = the moles of $C$ disappearing.
Then $x$ = the moles of $B$ combining with $x$ moles of $C$;
and $x$ = the moles of $A$ formed from this combination.

The new concentrations will be $(3 - x)$ moles of $C$, $(2 - x)$ moles of $B$, and $(1 + x)$ moles of $A$. Since only concentration and not temperature has been changed, the equilibrium constant $K$ will be the same both before and after $C$ has been added.

Now $$K_{\text{before}} = \frac{(\text{conc.}_B) \times (\text{conc.}_C)}{(\text{conc.}_A)} = \frac{2 \times 2}{1} = 4$$

And $$K_{\text{after}} = 4 = \frac{(\text{conc.}_B) \times (\text{conc.}_C)}{(\text{conc.}_A)} = \frac{(2 - x)(3 - x)}{(1 + x)}$$

$$4 + 4x = 6 - 5x + x^2$$

$$x^2 - 9x + 2 = 0.$$

This is a quadratic equation of the form $ax^2 + bx + c = 0$, the solution for which is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}.$$

In our problem $a = 1$, $b = -9$, and $c = 2$; and therefore

$$x = \frac{+9 \pm \sqrt{81 - 8}}{2} = \frac{9 - 8.54}{2} = 0.23$$

and the new concentrations will then be

$$\begin{array}{ccccc} A & \rightleftarrows & B & + & C \\ 1 + x & & 2 - x & & 3 - x \\ 1.23 \text{ moles} & & 1.77 \text{ moles} & & 2.77 \text{ moles.} \end{array}$$

This calculation shows us that if 1 mole of substance $C$ is added to an equilibrium mixture containing 1 mole of $A$, 2 moles of $B$, and 2 moles of $C$, the resulting mixture will not contain 1 mole of $A$, 2 moles of $B$, and 3 moles of $C$. Instead, reaction will take place; some of the added $C$ will be removed (LeChatelier's law) by reaction with $B$; and the final concentrations of the different substances will be 1.23 moles of $A$, 1.77 moles of $B$, and 2.77 moles of $C$.

The application of the **Principle of Mass Action** enables the industrialist to calculate simply and accurately the quantitative effect of adding reactants or products to a system in equilibrium.

For reactions of the type

$$A + A \rightleftarrows B + C,$$

such as in the reaction

$$2\text{HI} \rightleftarrows \text{H}_2 + \text{I}_2,$$

the equilibrium expression would be

$$K = \frac{(\text{conc.}_B)(\text{conc.}_C)}{(\text{conc.}_A)(\text{conc.}_A)} = \frac{(\text{conc.}_B)(\text{conc.}_C)}{(\text{conc.}_A)^2};$$

which, for the particular reaction cited, gives

$$K = \frac{(H_2)(I_2)}{(HI)^2}.$$

In this we see that the concentration of HI is raised to the power indicated by the number of HI molecules in the molecular equation. The same is true for all other reactions. Thus for the equilibrium discussed in section 211:

$$FeCl_3 + 3NH_4CNS \rightleftarrows Fe(CNS)_3 + 3NH_4Cl,$$

the equilibrium expression would be

$$\frac{(Fe(CNS)_3) \times (NH_4Cl)^3}{(FeCl_3) \times (NH_4CNS)^3} = K,$$

and it is possible to calculate quantitatively the increase in $Fe(CNS)_3$ upon adding either $FeCl_3$ or $NH_4CNS$. For if the concentration of $FeCl_3$ is made larger, $K$ can be kept constant only if the concentration of $NH_4CNS$ becomes smaller, or if the concentrations of $Fe(CNS)_3$ and of $NH_4Cl$ become larger. Actually both of these factors operate; and the deep red color of $Fe(CNS)_3$ becomes more intense upon adding the $FeCl_3$, as we have seen.

**214. Pressure and the Equilibrium Constant General Case.**—For gaseous reactions the concentrations of the reactants can be expressed as partial pressures, rather than as numbers of moles. In either case the equilibrium expression applies.

Consider the case of a quantity of gas confined in a vessel at 7 atmospheres of pressure at some fixed temperature. Let us assume that at equilibrium the partial pressures of the gases are

$$\begin{matrix} A & + & B & \rightleftarrows & C \\ \text{4 atmospheres} & & \text{1 atmosphere} & & \text{2 atmospheres.} \end{matrix}$$

If the vessel is provided with a piston, which is then moved inwards so that the volume occupied by the gas is halved, the resulting partial pressures at the instant of compression will be 8 atmospheres of $A$, 2 atmospheres of $B$, and 4 atmospheres of $C$. This assumes, of course, that no heat is generated by the moving piston. A *force* has been applied to the system (pressure). As a result, chemical reaction will occur to counteract this increase in pressure. **Equilibrium will shift to the right, where there are fewer molecules, lower pressure.** For if we let

$x$ = the increase, in atmospheres, of substance $C$,
then $x$ = the decrease of $B$, since it takes 1 volume of $B$ to form 1 volume of $C$;
and $x$ = the decrease of $A$, for the same reason.

The new partial pressures will be $(8 - x)$ atmospheres of $A$, $(2 - x)$ atmospheres of $B$, and $(4 + x)$ atmospheres of $C$. Since temperature has remained constant, the equilibrium constant will remain the same during the operation.

That is

$$K_{\text{before}} = \frac{p_C}{p_A \times p_B} = \frac{2}{4 \times 1} = \tfrac{1}{2}$$

$$K_{\text{before}} = \tfrac{1}{2} = K_{\text{after}} = \frac{(4 + x)}{(8 - x)(2 - x)}$$

$$(8 - x)(2 - x) = 2(4 + x).$$

Multiplying this out we get

$$x^2 - 12x + 8 = 0.$$

This is a quadratic equation of the type $ax^2 + bx + c = 0$, in which $a = 1$, $b = -12$, and $c = 8$. Solving for $x$ we obtain

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{12 - \sqrt{144 - 32}}{2} = \frac{12 - 10.58}{2} = 0.71.$$

$$\underset{\substack{7.29\\ \text{atmospheres}}}{A} + \underset{\substack{1.29\\ \text{atmospheres}}}{B} \rightleftarrows \underset{\substack{4.71\\ \text{atmospheres}}}{C}.$$

From this calculation we see that doubling the pressure more than doubles the pressure of $C$ in the equilibrium mixture, since it has been increased from 2 to 4.71 atmospheres. On the other hand, the pressures of $A$ and of $B$ have not doubled. In other words, the equilibrium has shifted to the *right.*

The above calculation is another illustration of how the expression for the equilibrium constant enables us to calculate quantitatively the effect of changing the concentrations in a system at equilibrium.

**215. Pressure and Equilibrium. Some Examples.**—Calculations using actual chemical reactions often involve cubic and higher order mathematical equations which lie beyond the scope of this text. However, we shall discuss one reaction semi-quantitatively.

*Problem.* Consider the gaseous reaction

$$2SO_2 + O_2 \rightleftarrows 2SO_3.$$

If an equilibrium mixture of these three gases is compressed, what shift in the partial pressures of these gases will occur?

*Answer.*—The equilibrium constant for this reaction will be given by

$$\frac{(p_{SO_3})^2}{(p_{SO_2})^2(p_{O_2})} = K.$$

Increasing the total pressure of the system increases the partial pressure of both numerator and denominator; but since the former is dependent on $p^2$ while the latter is dependent on $p^3$, the denominator will be affected more. That is, $(p_{SO_2})^2(p_{O_2})$ will grow larger than $(p_{SO_3})^2$. To keep $K$ constant, this necessitates a shift in the equilibrium to the right, producing more $SO_3$ at the expense of $SO_2$ and $O_2$.

**As a general rule when a gaseous mixture at equilibrium is compressed, chemical reaction occurs and the equilibrium shifts towards the side containing the smaller number of molecules.** See table 43.

TABLE 43. EFFECT OF PRESSURE ON EQUILIBRIUM

| Reaction | Number of Molecules Involved | Increased Pressure Produces More |
|---|---|---|
| $PCl_5 \rightleftarrows PCl_3 + Cl_2$ | $1 \rightleftarrows 2$ | $PCl_5$ |
| $3H_2 + N_2 \rightleftarrows 2NH_3$ | $4 \rightleftarrows 2$ | $NH_3$ |
| $2SO_2 + O_2 \rightleftarrows 2SO_3$ | $3 \rightleftarrows 2$ | $SO_3$ |
| $Cl_2 + H_2 \rightleftarrows 2HCl$ | $2 \rightleftarrows 2$ | No effect |

For this reason the industrialist wishing to prepare ammonia by the reaction

$$\underbrace{N_2 + 3H_2}_{\text{4 molecules}} \rightleftarrows \underbrace{2NH_3}_{\text{2 molecules}}$$

will employ high pressures. It was an appreciation of this principle which led Haber (1908–1914) to pressures of several hundred atmospheres in the catalytic production of ammonia from nitrogen in the air; a process which is today the fountainhead of synthetic fertilizers and explosives (**534**).

**216. Temperature and Equilibrium.**—We have already learned (**208**) that the rate of chemical reaction is approximately doubled for each 10° rise in temperature. For a reversible reaction, although an increase in temperature accelerates both the forward and the back reactions, it does so unequally so that the equilibrium is displaced.

For the reaction

$$\text{(left)} \qquad 2SO_2 + O_2 \rightleftarrows 2SO_3 + 2 \times 22{,}600 \text{ calories} \qquad \text{(right)}$$

a rise in temperature shifts the equilibrium towards the left. An equilibrium mixture of these three gases contains the following amounts of $SO_3$: at 400°, 89%; at 550°, 85%; at 645°, 60%; and at 900°, 0.01%. Obviously a manufacturer of $SO_3$ could not operate at high temperatures.

This special case of LeChatelier's Principle was formulated by Van't Hoff, and is known as his **Law of Mobile Equilibrium** which states that **if we heat a system in equilibrium, the equilibrium is displaced in the direction which consumes heat.**

To take another example, when phosphorus pentachloride is heated, it dissociates with absorption of heat (endothermic reaction):

$$PCl_5 + 30{,}000 \text{ cal.} \rightleftarrows PCl_3 + Cl_2.$$

At 200° and 760 mm., 51.5% of $PCl_5$ is present; but at 300°, only 3% of the pentachloride is present. As the reaction is endothermic, rise of temperature displaces the equilibrium forward.

**217. Dependence of Yield upon Rate of Reaction and Equilibrium.**—The industrial chemist is often caught between the horns of a dilemma. On the one hand the *rate of reaction, i.e.*, the rate at which the equilibrium state is reached, is favored by an *increase* in temperature. On the other hand, the *equilibrium* may so lie that the industrial product is favored by a *decrease* in temperature. This is the case for the oxidation of $SO_2$, as is illustrated in Fig. 91. The industrialist must strike a profitable balance between these two factors. That is, he cannot use too low a temperature or the gases will not react appreciably during the short period they are in contact with the catalyst. Conversely, he cannot employ too elevated a temperature since the equilibrium mixture at this higher temperature contains an unprofitably small percentage of $SO_3$. He chooses conditions somewhere between the two extremes, using contact time and medium temperature indicated at point A in the figure.

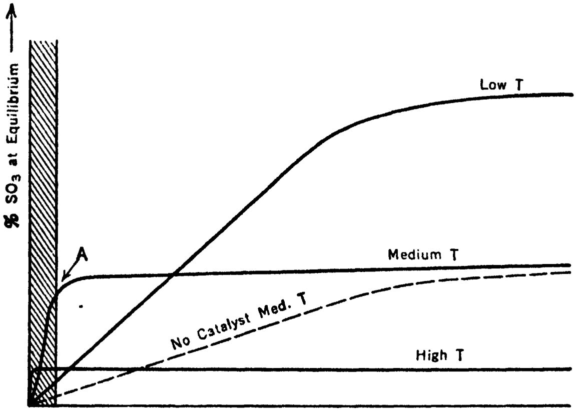


FIG. 91. Yield of $SO_3$ under different conditions. Suitable industrial contact time is in shaded area. Notice that medium temperature gives greatest yield of $SO_3$ in this time interval.

**218. Catalysis and Equilibrium.**—A catalyst always accelerates the forward and the back reactions equally. It does not, therefore, shift the equilibrium; it merely shortens the time necessary to attain equilibrium. This is illustrated in Fig. 91.

This fact is of considerable importance to the industrialist in his catalytic studies, inasmuch as the use of a catalyst enables him to operate at lower temperatures. For example, the percentage of $SO_3$ at equilibrium is higher at low temperatures, but reaction is too slow. The use of catalysts however speeds up the low temperature reaction sufficiently so that the process may be carried out at these lower temperatures where the equilibrium conditions are more favorable.

Also, the fact that the catalyst does not shift the equilibrium is of help in the preparation of good catalysts. The following experiments typify research which might be carried out to this end.

*Experiment 1.* A mixture of $SO_2$ and $O_2$ is heated at 400° C. for 1 day. At the end of this time the gases are found to contain 88.5% of $SO_3$.

*Experiment 2.* Pure $SO_3$ is heated at 400° C. for 1 day. At the end of this time the gases are found to contain 89.5% $SO_3$.

*Conclusion:* The equilibrium mixture of approximately 89% $SO_3$, 11% $SO_2$ plus $O_2$ has been approached from both sides, and represents the maximum yield of $SO_3$ which can be obtained by a theoretically perfect catalyst at 400° C.

*Experiment 3.* Pure $SO_2 + O_2$ is passed into an oven at 400° C. and remains in contact with the catalyst at this temperature for 2 minutes. The exit gases are analyzed and it is found that 20% $SO_3$ has been formed.

*Experiment 4.* A better catalyst is prepared. Treatment as in experiment 3 yields an off-gas containing 50% $SO_3$.

*Experiment 5.* A still better catalyst is discovered. In this case the off-gas contains 86% $SO_3$. The industrialist realizes that even a perfect catalyst could not bring the $SO_3$ yield above 89%, which is the equilibrium value determined in experiments 1–2; so the quest for a suitable catalyst is ended.

## IONIC EQUILIBRIUM

**219. Mass Action Expression.**—The foregoing discussion on equilibrium applies equally well to the reversible reactions which occur when electrolytes are ionized. For example, the mass action expression for the ionization of acetic acid (written $CH_3COOH$, or $HC_2H_3O_2$, or HAc):

$$HC_2H_3O_2 \rightleftarrows H^+ + (C_2H_3O_2)^-,$$

is

$$\frac{(H^+)(C_2H_3O_2^-)}{(HC_2H_3O_2)} = K_{\text{ionization}}.$$

**K is called the Ionization Constant.**

***Problem.*—An 0.1 molar solution of acetic acid is 1.34% ionized (186). What is the ionization constant, $K_{\text{ionization}}$?**

*Answer.*—As the fraction ionized is 0.0134, the molar concentration of each of the ions is 0.1 × 0.0134 = 0.00134, and the concentration of the non-ionized acid is 0.1 − 0.00134 = 0.09866; therefore,

$$K = \frac{(H^+)(C_2H_3O_2^-)}{(HC_2H_3O_2)} = \frac{(0.1 \times 0.0134)^2}{(0.09866)} = 0.0000182.$$

**220. Common Ion Effect.**—The formation of ferric ferrocyanate (211) may be written in the ionic form

$$Fe^{+++} + 3Cl^- + 3NH_4^+ + 3CNS^- \rightleftarrows \mathbf{Fe(CNS)_3} + 3NH_4^+ + 3Cl^-,$$

which may be abbreviated to

$$(\text{left}) \qquad \underset{\text{reddish-brown}}{Fe^{+++}} + \underset{\text{colorless}}{3CNS^-} \rightleftarrows \underset{\text{deep red}}{Fe(CNS)_3}. \qquad (\text{right})$$

DEMONSTRATION 79. SHIFTING IONIC EQUILIBRIUM

Materials: Three beakers, three stirring rods, solution containing 2000 cc. water plus 20 cc. N/10 $FeCl_3$ plus 20 cc. N/10 $NH_4CNS$; solid or concentrated solutions of several ferric salts and several thiocyanates.

The addition of either $Fe^{+++}$ or $CNS^-$ will shift the equilibrium to the right, intensifying the color as deep red $Fe(CNS)_3$ is formed. It does not matter what ferric salt or thiocyanate is added; only **the substances added must have an ion in common with one of the reacting species.** This is known as the **common ion effect.**

The common ion effect involves a very general and important principle in analytical chemistry. Because of it, the concentration of any ion can be controlled. Thus the degree of ionization of any substance may be repressed by adding to its solution a substance which supplies a large amount of a common ion.

DEMONSTRATION 80. COMMON ION EFFECT

Materials: $NH_4OH$, solid $NH_4Cl$, phenolphthalein indicator solution, beaker, stirring rod.

A few drops of a solution of phenolphthalein are added to some very dilute ammonium hydroxide. A deep purple-red color indicates the presence of the hydroxide-ion ($OH^-$). When $NH_4Cl$ is added to the liquid, the color disappears. This is because the highly ionized $NH_4Cl$ supplies $NH_4^+$ ions and drives the following reaction to the right, forming molecules of $NH_4OH$:

$$NH_4^+ + OH^- \rightleftarrows NH_4OH.$$

The addition of $NH_4Cl$ therefore represses the ionization of $NH_4OH$.

**221. Solubility Product.**—Let us consider a beaker containing a saturated solution of an electrolyte, *AB*, with solid *AB* in contact with the solution. Ions and dissolved molecules are in chemical equilibrium in the solution; and there is also a physical equilibrium between dissolved and undissolved molecules. At any given temperature, the concentration of *AB* molecules in solution is therefore fixed at some constant value $K_{AB}$. In such a case the equilibrium expression simplifies to give a special kind of equilibrium constant known as the **solubility product.**

$$AB \rightleftarrows A^+ + B^-$$

$$\frac{(A^+)(B^-)}{(AB)} = \frac{(A^+)(B^-)}{K_{AB}} = K,$$

whence $$(A^+) \times (B^-) = K \cdot K_{AB} = K_{\text{S.P.}}$$

For example the

$$K_{\text{S.P. of AgCl}} = (Ag^+) \times (Cl^-),$$
$$K_{\text{S.P. of PbCl}_2} = (Pb^{++}) \times (Cl^-)^2,$$
$$K_{\text{S.P. of As}_2\text{S}_3} = (As^{+++})^2 \times (S^{=})^3.$$

Solubility product is an index of the actual solubility of the substance. Very slightly soluble substances, such as AgCl, $BaSO_4$, and $CaCO_3$, have very low solubility products, while more soluble substances (*e.g.*, $KClO_3$ and NaCl) have higher. The value of the solubility product varies greatly, therefore, with different salts.

**222. Solubility Product and Common Ion Effect.**—The common ion effect operating in conjunction with solubility product is the basis of qualitative analysis; for it determines the conditions under which an unknown ion may be precipitated out. For example, silver chloride has a very low solubility product. This means that the product $(Ag^+) \times (Cl^-)$ can never be large. If a solution containing a moderate quantity of silver ion is added to a solution containing a moderate quantity of chloride ion, the combined $(Ag^+) \times (Cl^-)$ is much greater than the solubility product permits; molecules of AgCl are formed and silver chloride precipitates. If the analyst wishes to remove practically all of the silver from solution, he adds an **excess of $Cl^-$.** The product $(Ag^+) \times (Cl^-)$ must still remain constant; this can be done only at the expense of the $Ag^+$, so that the addition of excess $Cl^-$ precipitates silver chloride.

### DEMONSTRATION 81. SOLUBILITY PRODUCT

Materials: Three test-tubes; crystals of $AgNO_3$, $NaC_2H_3O_2$ and $NH_4NO_3$; saturated solution of $AgC_2H_3O_2$.

A crystal of silver nitrate is dissolved in the saturated solution of silver acetate; in a short while *silver acetate* precipitates out. In a second tube, solid sodium acetate added to silver acetate likewise precipitates *silver acetate.* In the third tube, ammonium nitrate has no effect on a saturated solution of silver acetate. This is an example of common ion effect operating in conjunction with solubility product.

$$\text{(left)} \qquad AgC_2H_3O_2 \rightleftarrows Ag^+ + C_2H_3O_2^-. \qquad \text{(right)}$$

Addition of a common ion, either silver ion or acetate ion, drives the reaction to the left; forming more silver acetate molecules. In the saturated solution, the product $(Ag^+) \times (C_2H_3O_2^-)$ is exactly equal to the solubility product. The addition of either more silver ion or acetate ion increases the **ion-product** $(Ag^+) \times (Cl^-)$ to greater than the solubility product; so silver acetate precipitates. Since $NH_3NO_3$ does not possess a common ion, it has no effect upon the silver acetate.

This principle is the basis of most of the reactions in analytical chemistry, by which complete removal of any ion can be achieved.

## DRIVING REACTIONS TO COMPLETION

**223. Irreversible Reactions.**—So far in this chapter we have discussed only reversible reactions. This means that the potential energy hump, the energy of activation, is not inordinately high above the initial and final troughs (**191**). For if the back reaction has too high an energy of activation, it will not take place, and reaction will occur only in the forward direction. In this case, the reaction is **irreversible.** For example magnesium burns in oxygen to form magnesium oxide; but the oxide does not dissociate appreciably until very high temperatures are attained, *i.e.*, until sufficient energy of activation is supplied. That is why the linings of furnaces and kilns are made of magnesium oxide. Lime is another refractory material which does not readily undergo decomposition.

**224. Driving Reactions to Completion.**—A reaction which is normally reversible may be driven almost entirely in one direction by changing the concentration of the reacting species. In this event the reversible reaction behaves essentially like an irreversible reaction.

**a. Increasing the concentration of one of the reactants may drive reaction to completion.**

In Section 222 we learned of the use of an excess of $Cl^-$ to remove effectively traces of $Ag^+$ from solution, driving the reaction practically to completion to the right. A quantitative yield of silver chloride can be obtained upon treating with hydrochloric acid a solution containing silver ions. In analytical chemistry this device finds wide-spread application whenever it is necessary to remove traces of foreign ions.

**b. Removing a product as a gas may drive reaction to completion.**

Thus quicklime (CaO) is manufactured by heating limestone ($CaCO_3$) in kilns:

$$\mathrm{CaCO_3} \rightleftarrows \mathrm{CaO} + \mathrm{CO_2} \uparrow .$$

The gaseous product, $CO_2$, is removed or allowed to escape, so the reaction has a tendency to run to completion to the right.

**c. Removing a product as a precipitate may drive reaction to completion.**

We have seen that, when aqueous solutions of silver nitrate and sodium chloride are mixed in the proper proportions, the reaction goes practically to completion, for insoluble silver chloride is formed:

$$\mathrm{Na^+} + \mathrm{Cl^-} + \mathrm{Ag^+} + \mathrm{NO_3^-} \rightarrow \mathrm{AgCl} \downarrow + \mathrm{Na^+} + \mathrm{NO_3^-}.$$

The essential change is the union of $Ag^+$ and $Cl^-$ to form a precipitate of AgCl.

**In general, when two ionized substances are mixed, the action may be carried to completion in case one of the products is an insoluble substance.**

The following plan may be adopted in the formulation of reactions of this type:

$$\begin{array}{lllclcl}
 & \mathrm{AgNO_3} & \rightleftarrows & \mathrm{Ag^+} & + & \mathrm{NO_3^-} & \\
 & \mathrm{NaCl} & \rightleftarrows & \mathrm{Cl^-} & + & \mathrm{Na^+}. & \\
 & & & \downarrow\uparrow & & \downarrow\uparrow & \\
\text{(dissolved)} & & & \mathrm{AgCl} & & \mathrm{NaNO_3} & \text{(dissolved)} \\
 & & & \downarrow\uparrow & & & \\
\text{(solid)} & & & \mathrm{AgCl} & & &
\end{array}$$

Note the number of equilibria. Since AgCl is practically insoluble in water, a very slight excess of NaCl will effect complete precipitation.

**d. Removing a product as a slightly ionized substance may drive reaction to completion.**

If NaOH is added to $NH_4Cl$ ammonia ($NH_3$) is driven off. This is due to the formation of slightly ionized $NH_4OH$, which dissociates into $NH_3$ and $H_2O$. The sequence of reactions is represented below, and takes place almost wholly to the right:

$$\begin{aligned} NaOH + NH_4Cl &\rightleftarrows NaCl + NH_4OH \\ & \qquad\quad \underset{\text{(slightly ionized)}}{NH_4OH} \rightleftarrows NH_3 + H_2O. \end{aligned}$$

**225. Summary.**—In this chapter we have learned that rate of reaction depends upon the concentration of the reacting species (pressure of gas, concentration in solution, etc.), and upon the energy (temperature, light, etc.), necessary to bring reaction about.

If reversible, the reaction may be favored in one direction more than in another by altering these factors. Increased temperature shifts the equilibrium so as to consume heat. Increased pressure shifts the equilibrium to the side where there is the fewest number of molecules. A mathematical formulation, known as the equilibrium constant expression, permits quantitative calculations of the effect which temperature, pressure, etc., will have in shifting equilibrium: such calculations are of obvious value to the industrialist. The role of catalyst in these reactions is to increase rate of reaction; the catalyst, however, does not shift equilibrium.

Reactions in solution, taking place between ions, are subject to the same rules which govern molecular or gaseous reactions. The equilibrium constant for ions is known as the ionization constant. In a saturated solution the product of the respective ions, raised to the powers represented by their numbers in the equation, gives a number known as the solubility product. This latter is valuable in analysis, where complete removal of some ion is desired.

Removal of substances represented by one side of the equation will drive the reaction towards that side; and complete removal of these products drives the reaction to completion to that side.

**Reading References:** Articles number 53, 56, 209 and 403 in the Appendix.

## QUESTION REVIEW

I. RATE OF REACTION (207). **Influence of concentration, P and T (208).**

1. Describe the iodine clock experiment. Explain it in terms of the relative rates of the three reactions involved.
2. Draw a potential energy curve for a chemical reaction. Show what is meant on the curve by energy of activation, potential energy hump, heat of reaction, initial and final states.
3. Explain the difference between the *total mass* of material and its *active mass*.
4. Explain why food keeps better on ice. Explain this in terms of the Maxwellian curve for distribution of energy.

II. CHEMICAL EQUILIBRIUM. FACTORS SHIFTING EQUILIBRIUM (209–210).

**a. Concentration (211). Mass action (212, 213).**

5. Describe an experiment illustrating that change in concentration shifts equilibrium.
6. Write the mass action expressions, showing the equilibrium constants for the following reactions:

$$PCl_5 \rightleftarrows PCl_3 + Cl_2; \quad N_2 + 3H_2 \rightleftarrows 2NH_3;$$
$$4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2.$$

7. Substance A dissociates reversibly into substances B and C. At a fixed temperature, the equilibrium mixture contains 1 mole of A, 2 moles of B, and 1 mole of C. If an additional mole of C is added, what will the new concentrations of the three substances be? (Make use of the quadratic expression in section 213.)

**b. Pressure and the equilibrium constant (214, 215).**

8. Substance A dissociates reversibly into substances B and C. At a certain temperature the equilibrium mixture contains 1 atmosphere each of the three gases. What will their partial pressures be if the gas mixture is compressed to half this original volume?
9. Explain why pressure favors the yield of ammonia in the reaction:

$$N_2 + 3H_2 \rightleftarrows 2NH_3.$$

10. At equilibrium, experiment showed that there were in a liter 3 moles of $SO_2$, 1 mole of $O_2$, and 2 moles of $SO_3$. Find the equilibrium constant, *K*.

    *Note.* $2SO_3 \rightleftarrows 2SO_2 + O_2$. *Ans.*, 2.25.

11. If 5 moles of $O_2$ and 2 moles of $SO_3$ are in equilibrium with $SO_2$, find the molecular concentration of $SO_2$. Equilibrium constant for equation above is 2.25. *Ans.*, 1.34.

12. State the general rule for the effect of pressure upon equilibrium. Which reactions in Table 38, page 239, are more sensitive to changes in pressure?

**c. Temperature (216). Rate of reaction (217).**

13. In case of the chemical reactions represented by the following equations, show the effect of rise of temperature upon the equilibrium point:

    (1) $3O_2 + 61{,}400 \text{ cal.} \rightleftarrows 2O_3$.
    (2) $4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2 + 28{,}000 \text{ cal.}$
    (3) $N_2 + O_2 \rightleftarrows 2NO - 43{,}200 \text{ cal.}$

    When chlorine is manufactured by Deacon's process, why is the yield greater at 370° than at 450°?

14. Plot curves for a number of temperatures showing how the yield of an industrial product depends upon (*a*) rate of reaction; (*b*) concentration of the product at equilibrium.

**d. Catalyst: does not shift equilibrium (218).**

15. Insert curves for the effect of catalysts in the graph drawn for question 14. Discuss the function of catalysts in industry.

III. IONIC EQUILIBRIUM. **Ionization constant (219). Common ion (220). Solubility product (221, 222).**

16. Write the expression for the ionization constant for each of the following substances: $NaCl$, $Al_2(SO_4)_3$, $(NH_4)_2SO_4$.
17. Show how the degree of ionization of $H_3PO_4$ may be lowered by an application of the common ion effect.
18. Write the solubility product expressions for the following substances: $As_2S_5$, $BaSO_4$, $CaSO_4$, $PbCl_2$, $AgBr$, $PbI_2$.
19. Describe an experiment with silver acetate which illustrates: saturated solution, solubility product, ion product, and common ion effect.

IV. DRIVING REACTIONS TO COMPLETION (223–224).

20. Describe in terms of potential energy curves why some reactions are essentially irreversible.
21. Why are magnesium oxide and silicon dioxide bricks used for lining high temperature furnaces?
22. How may a quantitative yield of silver chloride be obtained from a solution containing silver ion?
23. Under what conditions may cooling the product drive a reaction to completion?
24. Give equations illustrating reactions being driven to completion by the formation of (*a*) a precipitate; (*b*) a slightly ionized substance; (*c*) a gas.

**Summary (225).**

## CHAPTER XVIII

# OXIDATION AND REDUCTION. ACIDS AND BASES

### TRANSFER OF ELECTRONS

**226. Oxidation and Oxidizing Agents.**—We have seen (42) that various compounds part with oxygen more or less readily and therefore act as oxidizing agents.

DEMONSTRATION 82. OXIDIZING AGENT

Materials: Solid $KNO_3$, powdered charcoal, 50 mm. porcelain evaporating dish over burner.

When potassium nitrate is heated in an evaporating dish, the oxygen which is liberated will ignite particles of charcoal (carbon) dropped into it. Sparks fly.

$$2KNO_3 \rightarrow 2KNO_2 + O_2$$
$$O_2 + C \rightarrow CO_2.$$

Some important oxidizing agents and the products which they form are tabulated below.

TABLE 44. SOME OXIDIZING AGENTS AND THEIR PRODUCTS

| Oxidizing Agents | Examples | Products Usually Formed |
|---|---|---|
| Peroxides | $H_2O_2$, $Na_2O_2$, BaO | $H_2O$, NaOH, $Ba(OH)_2$ |
| Dioxides | $MnO_2$, $PbO_2$ | $Mn^{++}$, $Pb^{++}$ |
| Nitrates | $HNO_3$, $KNO_3$ | $NH_3$, NO, $NO_2$, $KNO_2$ |
| Chlorates | $KClO_3$ | $KClO_2$, KCl |
| Permanganates | $KMnO_4$ | $Mn^{++}$, $K^+$, ($O_2$) |

**Warning:** *Never grind or heat oxidizing agents with combustible materials, such as $KClO_3$ with C or S.*

Ordinary gunpowder is a mixture of sulfur, charcoal (carbon), and potassium nitrate. In this case we have an oxidizing agent mixed with two combustible materials; so when a gun is discharged, combustion is supported by oxygen liberated from potassium nitrate, and is not dependent upon the oxygen of the atmosphere. Large volumes of gases, such as $CO_2$ and $SO_2$, are formed at a very high temperature; therefore the cannon-ball is projected from the gun with great velocity.

Potassium chlorate, when heated sufficiently, gives up all its oxygen, forming potassium chloride. $KClO_3$ is a powerful oxidizing agent and as such is used in the manufacture of matches, fireworks, and explosives.

**227. Reduction and Reducing Agents.**—A reducing agent robs a substance of oxygen. Some important reducing agents follow.

TABLE 45. SOME REDUCING AGENTS AND THEIR PRODUCTS

| Reducing Agents | Examples | Products Usually Formed |
|---|---|---|
| Carbon | C | CO, $CO_2$ |
| Lower oxides | CO, $SO_2$ | $CO_2$, $SO_3$ |
| Water gas | $H_2$, CO | $H_2O$, $CO_2$ |
| Hydrogen compounds | $H_2S$, HI, $H_2SO_3$ | $H_2SO_4$, $I_2$, $H_2SO_4$ |
| Metals | H, Na, Al, Mg | oxides |
| Ferrous compounds | FeO, $FeSO_4$ | $Fe_2O_3$, $Fe_2(SO_4)_3$ |

Carbon (coke, charcoal) and carbon monoxide are our most important reducing agents for liberating the metals from their ores or oxides. Thus, cuprite (cuprous oxide), $Cu_2O$, is an ore of copper. It may be reduced by heating with carbon:

$$2Cu_2O + C \rightarrow 4Cu + CO_2.$$

Our most important iron ore is hematite, $Fe_2O_3$. It is reduced in a blast furnace by means of carbon and carbon monoxide:

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO,$$
$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2.$$

Zinc oxide, ZnO, is also reduced by means of carbon:

$$ZnO + C \rightarrow Zn + CO.$$

Magnesium reduces $SiO_2$, and aluminum reduces such oxides as $Cr_2O_3$, $Fe_2O_3$, and $MnO_2$:

$$SiO_2 + 2Mg \rightarrow 2MgO + Si,$$
$$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr.$$

These reductions take place at very high temperatures.

**228. Electron Transfer during Oxidation-Reduction.**—In a broader sense oxidation-reduction is said to have taken place whenever there is a change in valence. In such cases the substance which increases in valence is said to have been oxidized; the substance which is reduced in valence is said to have been reduced. These valence changes involve the give-and-take of electrons; one cannot occur without the other; oxidation must always accompany reduction.

When magnesium ribbon burns, a transfer of electrons takes place:

$$\begin{array}{c} 2\mathrm{Mg}^0 + \mathrm{O}_2^0 \rightarrow 2\mathrm{Mg}^{++}\mathrm{O}^{=}. \\ \downarrow \qquad \uparrow \\ 2 \times 2e \;=\; 4e \end{array}$$

Another simple illustration is the formation of *sodium chloride* by the direct combination of its constituents. The reaction may be formulated thus:

$$\begin{array}{c} 2\mathrm{Na}^0 + \mathrm{Cl}_2^0 \rightarrow 2\mathrm{Na}^{+}\mathrm{Cl}^{-}. \\ \downarrow \qquad \uparrow \\ 2 \times 1e \;=\; 2e \end{array}$$

Electrons are no doubt transferred from the sodium to the chlorine atoms, the change being accompanied by the evolution of energy. The sodium atom is oxidized and the chlorine atom is reduced.

**Fundamentally, then, oxidation may be regarded as the loss of electrons, while reduction is the converse.**

All displacement reactions involve such a transfer of electrons, and are therefore oxidation-reduction reactions. The activity series of metals (45), which predicts whether displacement will take place or not, is an index of the relative tendencies of different metals to lose electrons to other metals. The more active metals lose electrons more readily. Thus iron loses electrons to copper in the following reaction:

$$\underbrace{\mathrm{Fe} + \mathrm{Cu}}_{2e}\mathrm{SO}_4 \rightarrow \mathrm{Cu} + \mathrm{FeSO}_4.$$

**229. Oxidation-Reduction Potentials.**—In a foregoing section (197) we saw that whenever a metal is immersed in a solution of one of its salts, a difference of electrical potential may be observed between the metal and the solution. This potential is a measure of two competing forces: the metal loses electrons and passes as an ion into solution, while the ions gain electrons and are deposited out as atoms, *viz.*,

$$\mathrm{Zn}^0 \rightleftarrows \mathrm{Zn}^{++} + 2e.$$

Since this potential difference is a measure of the tendency of the metal to lose electrons, it is evident that a comparison of the potentials produced by different metals immersed in solutions of their salts is also an index of their relative oxidizing and reducing properties. In fact, such a table is none other than the familiar electromotive force series, the activity series of the metals.

**In comparing these potentials, it is customary to use 1 molar solutions of salts, and to use as a standard the potential of hydrogen.** The latter is obtained by bubbling hydrogen at one atmosphere pressure past a platinized electrode immersed in a 1 molar acid solution.

### DEMONSTRATION 83. ELECTRODE POTENTIALS

Materials: Hydrogen electrode, strips or rods of copper, zinc, aluminum, silver; 1 molar solution of salts of these metals, voltmeter connected to electrode and metal.

The voltages obtained by the system $H_2/H^+ :: M^+/\text{Metal}$ may be demonstrated for a number of metals. Accurate determinations of these potentials are given in Table 46.

TABLE 46

Standard Potentials

1 M Solutions at 25° C.
Metal/Cation

| | | |
|---|---|---|
| K, | $K^+$ | +2.92 |
| Ca, | $Ca^{++}$ | 2.76 |
| Na, | $Na^+$ | 2.715 |
| Mg, | $Mg^{++}$ | 1.55 |
| Al, | $Al^{+++}$ | 1.33 |
| Zn, | $Zn^{++}$ | 0.762 |
| Fe, | $Fe^{++}$ | 0.441 |
| Cd, | $Cd^{++}$ | 0.401 |
| Ni, | $Ni^{++}$ | 0.23 |
| Sn, | $Sn^{++}$ | 0.136 |
| Pb, | $Pb^{++}$ | 0.122 |
| **$\frac{1}{2}H_2$,** | **$H^+$** | **0.000** |
| Cu, | $Cu^{++}$ | −0.344 |
| Ag, | $Ag^+$ | −0.799 |
| Hg, | $Hg_2^{++}$ | −0.799 |
| Au, | $Au^{+++}$ | −1.36 |

TABLE 47

Standard Potentials

1 M Solutions at 25° C.
Non-metal/Anion

| | | |
|---|---|---|
| $\frac{1}{2}F_2$, | $F^-$ | −2.85 |
| $\frac{1}{2}Cl_2$, | $Cl^-$ | −1.358 |
| $\frac{1}{2}Br_2$, | $Br^-$ | −1.085 |
| $\frac{1}{2}I_2(s)$, | $I^-$ | −0.535 |
| $\frac{1}{2}O_2$, | $OH^-$ | −0.440 |

The higher up in the table, the greater is the reducing activity of the metal, the more easily it *loses* electrons. This corroborates what we already know about the activity series of metals, namely that **any metal will displace any other metal below it in the series.**

For example, any metal above hydrogen will displace hydrogen from acids. Conversely, substances lower in the table are more readily reduced; copper, for example, is more readily obtained by reduction than are magnesium and zinc.

**Anion electrode potentials** may be obtained by methods more complicated than those for metals. Table 47 gives such results and indicates the ability of the free element to *gain* electrons. Thus chlorine will liberate iodine from iodides, the iodine losing an electron to the chlorine.

In addition to these standard potentials, for pairs consisting of the free element and its ion, **oxidation-reduction potential tables** have been constructed to show the potentials between two ions of different charge for the same element. These, too, indicate the readiness with which the element may be oxidized or reduced. Using 1 M solutions at 25° C. gives the values: $Pb^{++}$, $Pb^{+++}$ $- 1.75$; $Fe^{++}$, $Fe^{+++}$ $- 0.772$; $Cu^{+}$, $Cu^{++}$ $- 0.16$; and $Sn^{++}$, $Sn^{++++}$ $+ 0.15$.

## TRANSFER OF PROTONS

NOTE: A good deal of the remaining portion of the chapter is in fine print. This may be omitted at the option of the instructor.

**230. Acids and Bases.**—Reducing agents have, then, the chemical property of losing electrons; oxidizing agents have the chemical property of accepting electrons:

$$\begin{array}{l} \mathrm{Fe} + \mathrm{CuSO_4} \rightarrow \mathrm{Cu} + \mathrm{FeSO_4}. \\ \quad \searrow 2e \nearrow \end{array}$$

Fe is the reducing agent; it loses electrons to copper. This reaction involves a transfer of **electrons**, and is called an oxidation-reduction reaction.

There is another class of substances which has the chemical property of losing or accepting **protons** ($H^+$); these substances are called **acids** and **bases.** In the following reaction HCl acts as an acid, $H_2O$ acts as a base:

$$\begin{array}{l} \mathrm{HCl} + \mathrm{H_2O} \rightleftarrows \mathrm{H_3O^+} + \mathrm{Cl^-}. \\ \quad \searrow \mathrm{H^+} \nearrow \end{array}$$

Stated formally, if the reaction

$$A \rightleftarrows H^+ + B$$

can occur at all, $A$ may be called the **conjugate acid,** whatever its charge, and $B$ may be called the **conjugate base,** irrespective of the actual stoichiometrical course of the reaction. Together they form a **conjugate pair.**

In the foregoing reaction, HCl and $Cl^-$ form one conjugate pair; $H_3O^+$ and $H_2O$ form another.

A number of conjugate pairs are given in Table 48, where it will be noticed that acids include not only **neutral molecule acids** (HCl, $H_2SO_4$, $HNO_3$), but also **cation acids** ($NH_4^+$, $H_3O^+$) and **anion acids** ($HSO_4^-$, $H_2PO_4^-$); and that bases are similarly represented. $O^=$ and $OH^-$ are bases; while metallic hydroxides are salts (any ionic substance is a salt). Metallic hydroxides furnish the base $OH^-$ in aqueous solutions.

**231. Protolytic Reactions.**—Corresponding to oxidation-reduction reactions, which involve transfer of *electrons,* we have **protolytic reactions** which involve transfer of a *proton* from an acid to a base. Table 48 shows that a great many common reactions are really protolytic reactions.

TABLE 48. PROTOLYTIC REACTIONS

| General Form for a Protolytic Reaction | $A_1$ + | $B_2$ ⇄ | $A_2$ + | $B_1$ |
|---|---|---|---|---|
| **Ionization** is a protolytic reaction between a molecule and its solvent, resulting in the formation of ions | $HCl$<br>$H_2O$ | $H_2O$<br>$NH_3$ | $H_3O^+$<br>$NH_4^+$ | $Cl^-$<br>$OH^-$ |
| **Neutralization** is any protolytic reaction. | | | | |
| It may be salt-destroying | $H_3O^+Cl^-$ salt | $K^+OH^-$ salt | $2H_2O$ | $K^+Cl^-$ salt |
| It is not necessarily salt-destroying | $HCl$ | $H_2O$ | $H_3O^+$ a salt | $Cl^-$ |
| It does not necessarily involve water | $HCl$ | $CH_3COONa$ | $CH_3COOH$ | $Na^+Cl^-$ |
| The old definition of neutralization is represented by | $HX$ | $MOH$ | $H_2O$ | $MX$ |
| Heat of neutralization in aqueous solution is given by | $H_3O^+$ | $OH^-$ | $2H_2O$ | 13,780 cals. |
| **Salt-formation** is not always accompanied by the evolution of water | $CH_3CO^-OH^+$ | $C_2H_5CO^-ONa^+$ | $C_2H_5CO^-OH^+$ | $CH_3COO^-Na^+$ |
| **Addition reactions** are often protolytic reactions | $HCl$ | $NH_3$ | $NH_4^+$ | $Cl^-$ |
| **Levelling effect of water** is a protolytic reaction between strong acids and water to form the hydronium ion, the presence of which gives an appearance of equal strengths to acids whose strengths differ in non-aqueous solvents | $HCl$<br>$HNO_3$ | $H_2O$<br>$H_2O$ | $H_3O^+$<br>$H_3O^+$ | $Cl^-$<br>$NO_3^-$ |
| ...or between strong bases and water | $H_2O$ | $KNH_2$ | $NH_3$ | $K^+OH^-$ |
| **Displacement** of a weak acid by a strong one is useful in preparing salts of strong acids | $HNO_3$ | $CH_3COONa$ | $CH_3COOH$ | $NaNO_3$ |
| **Lyolysis** is a protolytic reaction between a cation acid or an anion base and the solvent. (Also **hydrolysis, ammonolysis**) | $NH_4Cl$<br>$H_2O$ | $H_2O$<br>$CH_3COONa$ | $H_3O^+ + Cl^-$<br>$CH_3COOH$ | $+NH_3$<br>$NaOH$ |
| **Protolytic catalysis** is a catalysis in which acids, bases or both act as catalysts by virtue of their undergoing protolytic reactions | $A_1 + (SH) + B_2$ | | $A_2 + (HS) + B_1$ | |

This latter reaction, protolytic catalysis, was one of the strongest arguments advanced by Brønsted and his co-workers (1923–1940) in support of this concept of acids and bases. Previously the term acid had been reserved for substances containing $H^+$, and bases for substances containing $OH^-$; and the concept of proton transfer was not involved. Acids, according to Arrhenius, were catalytically active in water because they furnished $H^+$ ions. But when Brønsted found that these same acids exhibited catalytic activity in non-aqueous solvents, where they could not ionize to give $H^+$ ions, the Arrhenius definition of acid was abandoned for the proton transfer concept. Proton transfer is free to occur in non-aqueous as well as aqueous media.

**232. Hydrogen Ion Concentration, pH.**—The ionization constant for the equilibrium

$$H_2O \rightleftarrows H^+ + OH^-,$$
$$\text{is} \ldots. K = C_{H^+} \times C_{OH^-},$$

the concentration of $H_2O$ being taken as constant. This product $C_{H^+} \times C_{OH^-}$ has the experimental value of $10^{-14}$ as determined by conductivity measurements. If acid is added to the water, this increases the $C_{H^+}$ (according to Brønsted it is $C_{H_3O^+}$, but for simplicity we shall refer only to the proton, $H^+$). Since the ion product must equal $10^{-14}$, an increase of $C_{H^+}$ leads to a decrease in $C_{OH^-}$. On the other hand, if $C_{OH^-}$ is increased, as may be done by adding a few drops of NaOH solution, $C_{H^+}$ must decrease. At all times the product of the two ion concentrations must equal $10^{-14}$. To express the concentrations of such solutions of acids and hydroxides by use of these exponentials is rather awkward; so that a system suggested by Sørenson in 1909 is employed. The expression pH (pronounced pee-aich), which is equal to $\frac{1}{\log_{10} C_{H^+}}$, is employed. For water, where $C_{H^+} = C_{OH^-}$, the pH of the solution is 7. In this case

$$C_{H^+} \times C_{OH^-} = 10^{-7} \times 10^{-7} = 10^{-14}.$$

For acid solutions, pH is less than 7; for alkaline solutions pH is between 7 and 14. A schematic representation of the variation of the $H^+$ and $OH^-$ concentrations is

| $OH^-$ | $OH^-$ | $OH^-$ | $OH^-$ | $OH^-$ |
|---|---|---|---|---|
| $H^+$ | $H^+$ | $H^+$ | $H^+$ | $H^+$ |

pH 1 2 3 4 5 6 7 8 9 10 11 12 13 14
pOH 13 ...... 7 ...... 1

ACID——————|——————BASIC

The pH of the blood is rigidly fixed between 7.35 and 7.5. Persons with pH above or below these limits are usually insane. Gastric juice, which contains dilute HCl, has a pH ranging between 1 and 2.5.

### DEMONSTRATION 84. pHs OF SOME SOLUTIONS

Materials: Methyl violet indicator, phenolphthalein indicator, 1 N solutions of HCl, $CH_3COOH$, $H_3BO_3$, $Na_2CO_3$, NaOH, $NH_4OH$; 0.1 N, 0.01, 0.001, 0.001 and 0.001 N solutions of $CH_3COOH$; 10 test glasses.

Methyl violet is an indicator which changes color over the pH range pH 1. to pH 3. Phenolphthalein indicator changes color at pH 9.6. The pH values of different acid and basic solutions (Demonstration 84) may be tested accordingly.

**233. Strength Exponent, pK.**—The electromotive force series indicates the ease with which an element loses electrons. It predicts, for example, that iron will displace copper from a solution of copper sulfate.

Analogously a scale of the relative strengths of acids and bases predicts the probable occurrence of a protolytic reaction. Unfortunately no absolute scale of acid and base strengths exists; for different solvents act differently upon acid and base ions of different charges.

However, so long as the discussion is limited to aqueous solutions, the ionization constant of the acid may be taken as an index of its strength. This ionization constant, which may be obtained by conductivity measurements, is called pK (pronounced pee-kay), the **strength exponent.** Table 49 gives the strength exponents for different conjugate pairs.

**234. Predicting Equilibria from pK.**—pK may be used to predict the extent of proton transfer in the same way that in oxidation-reduction reactions the electromotive force may be used to predict electron transfer. For if in the protolytic reaction

$$A_1 + B_2 \rightleftarrows A_2 + B_1$$

the tendency for the acid $A_1$ to lose its proton to $B_2$ is stronger than it is for $A_2$ to lose its proton to $B_1$, the reaction proceeds more to the right. This occurs when the strength of $A_1$ is much greater than the strength of $A_2$; that is, when $pK_{A_1} \ll pK_{A_2}$. Generalizing these conditions we may state that **any acid in the pK table will react more or less completely with any base below it in the table, but will react only slightly, if at all, with any base above it in the table.** The following reactions are predicted by this pK table.

Ionization complete..........$HCl + H_2O \rightleftarrows H_3O^+ + Cl^-$
very slight........$2H_2O \rightleftarrows H_3O^+ + OH^-$
Neutralization complete......$H_3O^+ + OH^- \rightleftarrows 2H_2O$
very slight........$CH_3COOH + Na^+Cl^- \rightleftarrows HCl + CH_3COONa$
Levelling effect of water complete.....................$HCl + H_2O \rightleftarrows H_3O^+ + Cl^-$

**235. pH of a Salt Determined by pK.**—The relative acid and base strengths of its constituent ions, as tabulated in the pK table, determine the pH of a salt.

### DEMONSTRATION 85. pHs OF SALTS

Materials: 12 test glasses, litmus paper, solutions of $K_3PO_4$, $Ca(HCO_3)_2$, $KHSO_3$, $MgSO_4$, NaCl, $NH_4Cl$, $AlCl_3$, $NH_4HSO_4$, $CH_3COONH_4$, $(NH_4)_2S$, $NH_4HSO_3$, KCN.

TABLE 49. STRENGTH EXPONENTS OF SOME CONJUGATE PAIRS

| Acid | Base | Strength Exponent (pK) |
|---|---|---|
| HCl (strong) | Cl (weak) | −7 |
| $H_2SO_4$ | $HSO_4^-$ | negative |
| $HNO_3$ | $NO_3^-$ | negative |
| $H_3O^+$ | $H_2O$ | −1.74 |
| $HSO_4^-$ | $SO_4^{=}$ | +1.7 |
| $H_2SO_3$ | $HSO_3^-$ | 1.77 |
| $H_3PO_4$ | $H_2PO_4^-$ | 2.12 |
| $Fe(H_2O)_6^{+++}$ | $Fe(H_2O)_5OH^{++}$ | 2.2 |
| $CH_3COOH$ | $CH_3COO^-$ | 4.75 |
| $Al(H_2O)_6^{+++}$ | $Al(H_2O)_5OH^{++}$ | 4.9 |
| $HSO_3^-$ | $SO_3^{=}$ | 5.3 |
| $H_2CO_3$ or $CO_2$ | $HCO_3^-$ | 6.51 |
| $H_2S$ | $HS^-$ | 7.1 |
| $H_2PO_4^-$ | $HPO_4^{=}$ | 7.23 |
| HClO | $ClO^-$ | 8 |
| HCN | $CN^-$ | 9.2 |
| $H_3BO_3$ | $H_2BO_3^-$ | 9.2 |
| $NH_4^+$ | $NH_3$ | 9.26 |
| $HCO_3^-$ | $CO_3^{=}$ | 10.34 |
| $H_2O_2$ | $HO_2^-$ | 11.7 |
| $HPO_4^{=}$ | $PO_4^{\equiv}$ | 12.46 |
| $HS^-$ | $S^{=}$ | 14.7 |
| $H_2O$ | $OH^-$ | 15.97 |
| $OH^-$ (weak) | $O^{=}$ (strong) | 24 |

Three reactions to litmus are possible. In the case of salts of sodium, potassium, calcium, barium and magnesium, the metals behave as such weak ions that the pH of the salt is determined by the nature of the anion present.

**a. The salt reacts neutral to litmus**

. . . if its acid and base ions are of approximately equal strength, *viz.*, $CH_3COONH_4$, $Al(H_2O)_6PO_4$.

. . . salts of the above metals if the anion is a very weak base, *viz.*, NaCl, $KNO_3$, $BaCl_2$, $MgSO_4$.

**b. The salt reacts acid to litmus, turning it pink**

. . . if it contains an *acid ion* which is stronger than the base ion, *viz.*, $NH_4\mathit{HSO_3}$, $\mathit{H_3O}Cl$, $\mathit{NH_4}Cl$, $\mathit{Al(H_2O)_6}Cl_3$.

. . . salts of the above metals, if the anion is stronger as an acid than as a base, *viz.*, $Na\mathit{HSO_4}$, $\mathit{KHSO_3}$, $Na\mathit{H_2PO_4}$.

**c. The salt reacts basic to litmus, turning it blue**

. . . if it contains a basic ion which is stronger than the acid ion, *viz.*, $(NH_4)_2\mathit{S}$, $Fe(H_2O)_3\mathit{(OH)_3}$, $\mathit{Al(H_2O)_5OH}Cl_2$.

. . . salts of the above metals, if the anion can be only a base, *viz.*, CaO, $Na_2S$, $K_3PO_4$, KCN, $BaCO_3$.

. . . salts of the above metals, if the anion is stronger as a base than as an acid, *viz.*, $Na_2HPO_4$, KSH, $Ca(HCO_3)_2$.

**236. Indicators.**—An indicator is any conjugate pair the conjugate acid of which differs in color from its conjugate base. Thus litmus changes color at pH 7 according to the protolytic equilibrium

$$\underset{\text{pink}}{\text{H Litmus}} + H_2O \rightleftarrows H_3O + \underset{\text{blue}}{\text{Litmus}}.$$

Just as different salts have different pH values, so different indicators change color at different pH values depending upon their strength exponents, pK.

DEMONSTRATION 86. INDICATOR COLOR CHANGE AT DIFFERENT pHs

Materials: 400 cc. beaker containing 10 cc. of 1 N sodium sulfite in water, burette containing 1 N sulfuric acid, phenolphthalein indicator, brom-cresol-green indicator, litmus paper.

The three indicators change color at different pHs: the phenolphthalein from red to colorless at pH 9.6, the litmus from blue to pink at pH 7.0, the brom-cresol-green from blue to yellow at pH 4.3. If sulfuric acid is added to sodium sulfite there is a gradual transition of pH from 10.6 to 1 as schematically represented:

$$\underset{\text{pH } 10.6}{Na_2SO_3} \rightarrow \underset{\text{pH } 4.3}{NaHSO_3} \rightarrow \underset{\text{pH } 2}{H_2SO_3} \rightarrow \underset{\text{pH } 1}{\overset{\text{excess}}{H_2SO_4}}$$

The phenolphthalein is first added, and the sulfuric acid run in until there is a color change; then litmus paper is put into the solution and the titration continued until the second color change occurs; finally the brom-cresol-green is added and the final color change brought about. This demonstrates that these indicators change color at entirely different pH values.

While it is beyond the scope of this text to elaborate, during the titration of a strong acid with a strong base the pH changes very rapidly in the neighborhood of pH 4 to 10 upon the addition of a single drop of excess acid or base; hence for all practical purposes titrations with several indicators give essentially the same end-point.

**237. Preparation of Pure Salts.**—The preparation of pure salts by the reaction

$$A_1 + B_2 \rightleftharpoons A_2 + B_1,$$

is considerably simplified if $B_2$ is a salt containing the lyate ion (a solvent molecule minus a proton). Thus in the preparation of lithium chloride in water solution we might

(*a*) use the lyate ion...........$HCl + LiOH \rightarrow LiCl + H_2O$,
(*b*) not use the lyate ion.......$HCl + CH_3COOLi \rightarrow LiCl + CH_3COOH$.

Obviously (b) would be more difficult to purify, since both water and acetic acid must be removed from the lithium chloride.

On the other hand, lithium chloride might be simply prepared in solvents other than water by employing the lithium lyate for $B_2$ in each case, *viz.*

$$\begin{array}{llll} HCl + LiOH & \rightarrow LiCl + H_2O & \text{in water} \\ HCl + LiNH_2 & \rightarrow LiCl + NH_3 & \text{in liquid ammonia} \\ HCl + \underset{\substack{\text{lithium}\\\text{lyate}}}{CH_3COOLi} & \rightarrow LiCl + \underset{\substack{\text{solvent}\\\text{is formed}}}{CH_3COOH} & \text{in glacial acetic acid.} \end{array}$$

## QUESTION REVIEW

I. TRANSFER OF ELECTRONS.

**a. Oxidation and oxidizing agents** (226).

1. Give the formulas for four oxidizing agents and the products which they form during oxidation.
2. Describe the composition and the working of gunpowder.

**b. Reduction and reducing agents** (227).

3. Give the formulas for four reducing agents and the products which they form during reduction.
4. Give three equations showing the use of reducing agents in the winning of metals from their ores.

**c. Electron transfer during oxidation-reduction** (228).

5. Write three equations illustrating displacement, and indicate the electron transfers involved.

**d. Oxidation-reduction potentials** (229).

6. Explain why the potential assumed by a metal immersed in a solution of its salt is a measure of its oxidizing-reducing properties.
7. Memorize and reproduce the order of metals and of non-metals in the potential tables.

II. TRANSFER OF PROTONS.

**a. Acids and bases** (230).

8. Define, also illustrate: proton, acid, base, conjugate pair, neutral molecule acid, cation base, cation acid, anion base, salt, protolytic reaction.

**b. Protolytic reactions** (231).

9. Give equations illustrating at least five types of protolytic reactions.
10. Why did Brønsted abandon the Arrhenius concept of acids?

**c. Hydrogen ion concentration, pH** (232).

11. Why is (pH + pOH) always equal to 14 in an aqueous medium?
12. Calculate the pH of each of the following solutions. It will be necessary to refer to a $\log_{10}$ table in answering this. 0.1, 0.001, 1 N HCl, considered completely ionized; 1 N $CH_3COOH$, considered 5% ionized.

**d. Strength exponent, pK (233). Predicting equilibria from pK (234). pH of a salt determined by pK (235).**

13. Name two conjugate pairs with a negative strength exponent, two in the vicinity of $H_3O^+$, four with strength exponents greater than 8.
14. By referring to the pK table, predict which of the following reactions will go to completion: $HCl + H_2O$; $KCN + H_2O$; $Fe(H_2O)_6Cl_3 + NaOH$; $NaHSO_3 + H_2SO_4$; $H_3PO_4 + HCN$.
15. What is the reaction of litmus to solutions of each of the following salts: $K_3PO_4$, $NH_4Cl$, $Al(H_2O)_6Cl_3$, $MgSO_4$, $NH_4HSO_3$, $KHSO_3$, $NaH_2PO_4$, $CaS$, $MgO$, $Fe(H_2O)_6NO_3$, $Ca(HCO_3)_2$, $CH_3COONH_4$, $CH_3COONa$?

**e. Indicators (236).**

16. Explain the color change of litmus in terms of a protolytic reaction.
17. Describe and explain the demonstration which shows that three indicators change color at different pHs.

**f. Preparation of pure salts (237).**

18. Give the formulas of the compounds used in preparing pure potassium chloride in (*a*) water; (*b*) liquid ammonia; (*c*) glacial acetic acid.

**Reading References:** Articles number 68, 73 and 423 in the Appendix.

# CHAPTER XIX

# ATOMIC STRUCTURE

## PART I. PHENOMENA CONNECTED WITH THE NUCLEUS

### A. NUCLEAR STRUCTURE OF THE ATOM

**238. The Electron.**—From time to time the **electron**, the unit negative charge of electricity, has been referred to. In our preliminary description (55), an atom was pictured as a nucleus surrounded by a planetary system of these electrons. This fact that electricity comes in discrete units, like grains of sand, became increasingly evident from researches during the past century.

For example, we employed the concept of the electron in explaining Faraday's second law of electrolysis in terms of the Arrhenius theory (175). Faraday has shown that a given quantity of electricity will deposit metals in the same proportion as their equivalent weights. Thus 23 g. of Na, 12 g. of Mg and 9 g. of Al, their respective equivalent weights, are deposited by 96,500 coulombs of electricity. We explained this by assuming that the positive charges of the metallic ions, $Na^+$, $Mg^{++}$, and $Al^{+++}$, were neutralized by 1*e*, 2*e*, and 3 electrons respectively. According to this picture, the number of metallic atoms electrodeposited by 1 electron would be, 1, $\frac{1}{2}$ and $\frac{1}{3}$ respectively for $Na^+$, $Mg^{++}$, and $Al^{+++}$; and this corresponds to the gram equivalent weights of these metals, 23/1 g., 24/2 g. and 27/3 g. (at. wt./valence).

Other evidence for the existence of the electron came from research on electric discharges in gases. Gas at low pressures conducts electricity, and a glow is produced in the neighborhood of the cathode. As the pressure is lowered below 0.01 mm. of mercury, the glow detaches itself from the cathode and moves down the tube leaving a so-called **Crookes dark space**, containing a stream of particles of electricity. Among other properties of these particles is their deflection in magnetic (Plücker, 1858) and electric (Goldstein, 1886) fields. From this it was established that their charge is negative; in fact this gaseous particle of electricity was held to be identical with the above mentioned electron, associated with ions in solution.

From the beginning of the twentieth century physicists busied themselves with measuring the weight and charge of an electron.

**The Millikan oil drop method for determining the charge, e, on an electron** is an excellent example of the methods employed. This novel experiment, concluded in 1913, won for its inventor, Robert A. Millikan, the Nobel Prize in Physics.

Oil is sprayed from an atomizer in an evacuated chamber. A short-focus telescope is pointed at *E*, Fig. 92; and when a drop of oil is observed to enter the lower chamber, *E* is closed. The lower chamber contains a large number of gaseous ions, produced by working an X-ray tube located outside the window $W_1$. The oil-drop picks up some of these gaseous ions, a dozen and more, and thereby becomes charged.

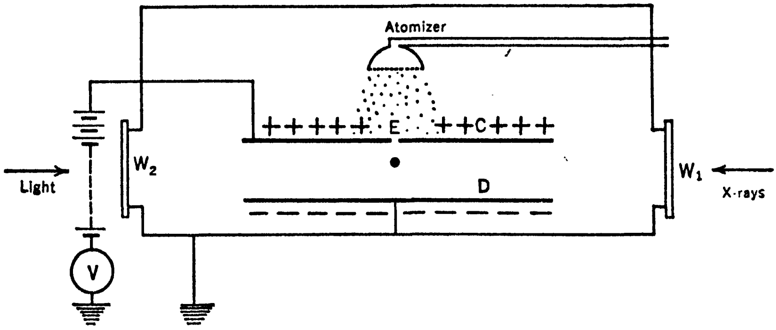


FIG. 92. The Millikan oil-drop method for determining the charge of an electron.

Two rates are then measured: (a) the rise of the droplet when a potential is applied to plate C and (b) the fall of the droplet under gravity. The latter has a constant value as given by the mass **m** of the drop times the constant of gravity, **g**, for falling bodies, *i.e., rate of fall* = **mg**. The *rate of rise* of the droplet depends upon the number of gaseous ions it has picked up. Mathematically it is composed of two factors: the downward pull (**mg**) of gravity, and the upward attraction ($Xe_n$) between the field strength **X** applied to C and the number of unit charges, $e_n$, on the oil drop. Combined, this gives

$$\frac{\text{rate of rise}}{\text{rate of fall}} = \frac{Xe_n - mg}{mg}.$$

In this equation **X** and **g** are known, the rates of rise and fall can be measured, and **m** can be calculated from the size and density of the drop. This leaves only $e_n$, which can therefore be calculated.

Careful measurements by the Millikan method have shown that the oil-drop picks up some multiple of $4.805 \times 10^{10}$ electrostatic units. This, then, is strong evidence that there is a unit of electric charge, the electron; and any multiple which Millikan obtained represented more than one unit charge picked up by the oil drop. For some time this method was accepted as the most accurate one for determining **e**, but of late other methods have replaced it.

**239. Wide Angle Deflection.**—Since atoms are electrically neutral, it was necessary to assume the presence of positive charges in the atom to neutralize the electrons. This led to a *jelly-fish* kind of atom depicted in Fig. 93, *a*.

However, in 1903 Lénard pointed out that since cathode rays (electrons) pass through thin aluminum foil, the aluminum atoms must be quite empty, otherwise the electrons would be deflected.

We shall see shortly, pages 298–299, that certain radioactive elements eject positively charged helium particles, called **alpha particles.** Geiger and Marsden showed (1909) that if a gold foil 0.0004 mm. thick is placed in the path of these alpha particles, 1 out of every 20,000 of the bombarding alpha particles does not pass through the foil, but instead is deflected back through a **wide angle** (Fig. 93, *b*). Examination of their work led Rutherford to the conclusion that the alpha particle could not have been deflected unless nearly the whole of the mass and positive charge of the gold atom were concentrated in a tiny nucleus surrounded by electrons (Fig. 93, *c*). Subsequent research has completely supported this conclusion. That the atom is, indeed, mostly empty space is confirmed by the current data which show that less than one million-millionth of the atom is solid matter; the rest is vacuity. The atom is therefore much more empty than our own solar system.

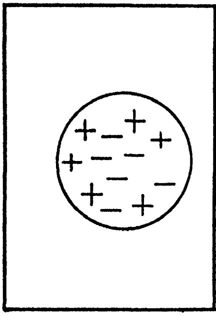


FIG. 93*a*. Jellyfish atom, before 1911.

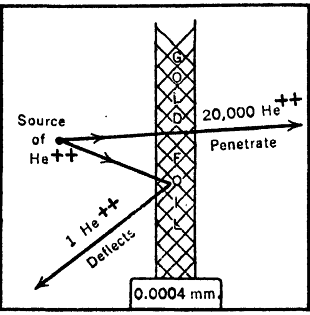


FIG. 93*b*. Geiger and Marsden wide-angle deflection experiment, 1909.

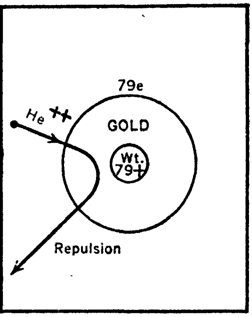


FIG. 93*c*. Nuclear atom, Rutherford's interpretation (1911) of wide angle deflection

**240. Rules of Structure.—**

**a. The atomic number equals the number of planetary electrons, the number and arrangement of which determine the chemical properties of the element.**

**b. The atomic number also equals the number of positive charges on the nucleus.**

**c. The atomic weight approximates the weight of the nucleus.**

The exact weight of the nucleus is determined by which isotope of the element is involved (**243**).

Examine, for example, the structures in Fig. 94.

*Problem:* ${}^{35}_{17}\mathrm{Cl}$ and ${}^{37}_{17}\mathrm{Cl}$ have what structures?

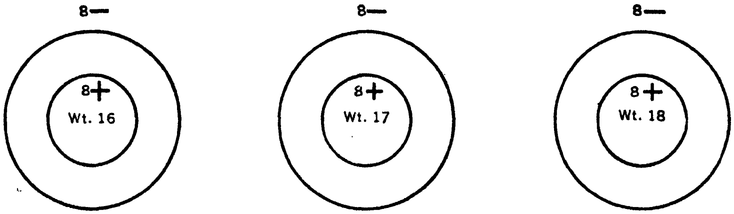


FIG. 94. Isotopes of oxygen.

**241. Particles Ejected from the Nucleus.**—When an atom is bombarded with swiftly moving missiles, such as alpha particles, other particles are ejected from the nucleus. Are these particles

TABLE 50. PARTICLES EJECTED FROM THE NUCLEUS

| Particle | Symbol | Charge | Approximate Mass (H = 1.0081) | Discoverer and Date |
|---|---|---|---|---|
| Electron | $e$ | $-1$ | $\frac{1}{1836}$ | G. Stoney (1891) proposes name. |
| Alpha particle | ${}^{4}_{2}\mathrm{He}$ | $+2$ | 4.0011 | E. Rutherford (1909); Soddy (1903). |
| Proton | ${}^{1}_{1}\mathrm{H}$ | $+1$ | 1 | E. Rutherford (1919). |
| Neutron | ${}^{1}_{0}n$ | 0 | 1 | Bothe and Becker (1930); J. Chadwick (1932). |
| Positron | $+e$ | $+1$ | $\frac{1}{1836}$ | C. Anderson (1932). |

Other particles of lesser importance are the **neutretto** and the **neutrino**, postulated on theoretical grounds. The **meson**, sometimes called the heavy electron or mesotron, charge $-1$, weight 50 to 200 times an electron, was discovered by Anderson of California in 1938, and fifteen days later by Street of Harvard.

present as such in the nucleus? To date it is not definitely known. The particles which have been identified as coming from the nucleus are given in Table 50.

**242. C. T. R. Wilson Fog-Track Apparatus.**—The most important instrument for identifying these ejected nuclear particles is the **fog-track apparatus**, invented by C. T. R. Wilson in 1911. In principle the particles are shot into a chamber supersaturated with water vapor; this water vapor condenses to a visible cloud upon the particle, or upon ions which the particle may form along its path; and the "cloud" thus formed may be photographed (Fig. 95).

When, on a frosty morning, we "see our breath," we are seeing myriads of water droplets which have condensed upon dust in the air. Without dust nuclei there would be no fog.

DEMONSTRATION 87. FORMATION OF FOG

Materials: Heavy 1-liter flask containing a little water, and provided with a three-way stop-cock leading (a) to a water vacuum pump and (b) to a large calcium chloride tube filled with cotton to filter out dust. Brightly illuminate the flask, and provide a black background.

The flask is evacuated. Upon suddenly admitting ordinary air, a fog forms in the flask. If, on the other hand, dustless air is admitted, no fog forms.

Now water vapor will condense not only on dust, but upon ions as well. The C. T. R. Wilson Cloud Chamber is filled with air supersaturated with water vapor; and the passage of any of the particles in Table 50 will supply ions upon which the water condenses. Different particles give characteristic fog-tracks (Fig. 96, *a–c*). Heavy alpha particles plough straight through the gas space and give tracks which are straight lines (Fig. 96, *a*). Particles which are much lighter, such as electrons or positrons, are deflected by collisions during their passage, and give a wobbly track (Fig. 96, *a*). If one side of the apparatus is charged positively, the fog-track of electrons will bend towards that side; fog tracks of a positron on the other hand bend in the opposite direction. From the amount of repulsion, or attraction, the weight of the particle may be calculated. Finally, whenever there is a collision within the chamber resulting in the formation of several new particles, this gives a Y-shaped pattern (Fig. 96, *b*). The lengths of the limbs of the Y, indicating the relative recoils of the two new particles, is a measure of the relative weights of these

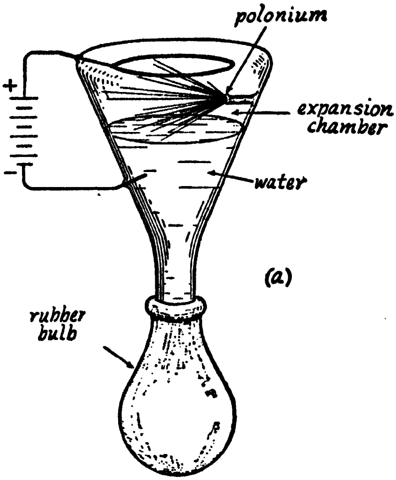


FIG. 95. Fog-track chamber.

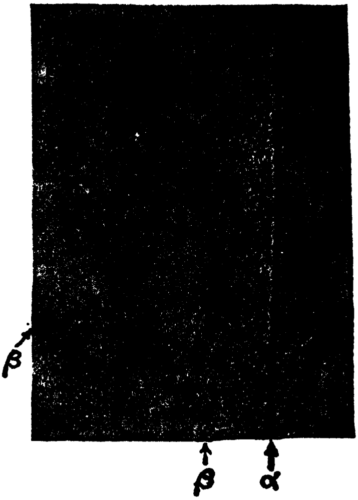


FIG. 96*a*. Rays of $\alpha$ and $\beta$ particles.

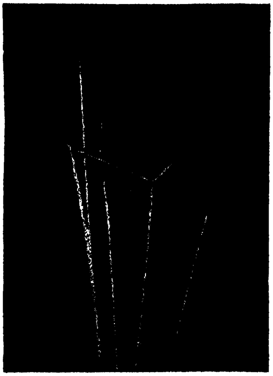


FIG. 96*b*. Fog-track of a transmutation.

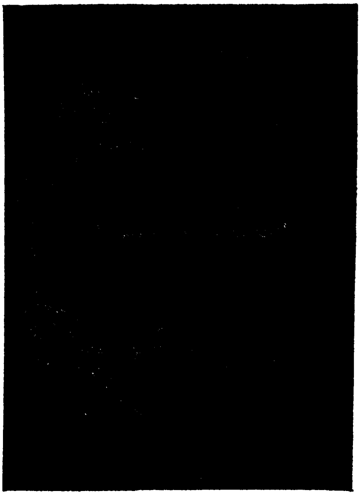


FIG. 96*c*. Fog-track of uranium fission.

new particles. This latter observation is particularly important in identifying the transmutations of elements (255).

## B. ISOTOPES

**243. Some Isotopes.**—If neutrons or protons, weights approximately 1, are the building blocks of atoms, we should expect the atomic weights to be whole numbers. While this is true for a number of atoms, chlorine, atomic weight 35.457, is a glaring exception. Experiment has furnished an explanation for this perplexing problem. Ordinary chlorine is a mixture of *two* kinds of atoms, one with atomic weight 35 and the other 37, and in just the correct ratio to give a composite weight of 35.457. These two atoms are called **isotopes** of chlorine (113).

While the atomic weights of these atoms differ, the atomic number is identical. Since this atomic number determines the number and arrangement of planetary electrons, which in turn determine the chemical properties of chlorine, we can understand why **the chemical properties of these isotopes are identical.**

Isotopes of any given element therefore have essentially the same chemical properties; they occupy the same place in the periodic table (**283**) since they have the same atomic number; but their atomic weights differ. That the number of planetary electrons is the same, but the atomic weights are different, is shown in Fig. 94.

There are over 250 isotopes known. See Table 51.

**244. Heavy Isotopes.**—The discovery of heavy hydrogen by Urey 1931 (52) and the fruitful biological, as well as chemical, research which followed its preparation in considerable quantities, intensified the efforts of chemists during the period 1932–1941 to prepare other heavy isotopes for "tagging" chemical reactions. By the end of 1940 heavy isotopes of hydrogen ($^{2}H$), oxygen ($^{18}O$), carbon ($^{13}C$), sulfur ($^{34}S$), and nitrogen ($^{15}N$), the most important tags for biological processes, had been prepared in quantities.

**Concentration of Heavy Isotopes.**—The methods for concentrating these isotopes is of some interest. The earliest attempt was, naturally, by use of the mass spectrograph by which isotopes had first been discovered. All the particles arriving at some predetermined spot on the photographic plate have the same mass; hence, by placing a suitable collector at this spot, the isotope should be isolable. However, a great many technical difficulties were encountered. By an improvement of mass spectrograph technique W. R. Smythe in 1934 was able to separate the three potassium isotopes $^{39}K$, $^{40}K$, and $^{41}K$; and to demonstrate that $^{40}K$ was radioactive. In 1939 O. Nier employed his specially simplified mass spectrometer in separating traces of $^{235}U$ from a

TABLE 51. PARTIAL TABLE OF ISOTOPES *

In order of decreasing abundance of each element. Isotopic weights are rounded off to the exact whole number.

| Element | Atomic Number | Chemical Atomic Wt. | Masses of Isotopes |
|---|---|---|---|
| H | 1 | 1.0080 | 1, 2, 3 |
| Li | 3 | 6.940 | 7, 6 |
| Be | 4 | 9.02 | 9, 8 |
| B | 5 | 10.82 | 11, 10 |
| C | 6 | 12.01 | 12, 13 |
| N | 7 | 14.008 | 14, 15 |
| O | 8 | 16.0000 | 16, 18, 17 |
| Ne | 10 | 20.183 | 20, 22, 21 |
| Mg | 12 | 24.32 | 24, 25, 26 |
| Si | 14 | 28.06 | 28, 29, 30 |
| S | 16 | 32.06 | 32, 34, 33 |
| Cl | 17 | 35.457 | 35, 37 |
| A | 18 | 39.944 | 40, 36, 38 |
| K | 19 | 39.096 | 39, 41, 40 |
| Ca | 20 | 40.08 | 40, 42, 43 |
| Cr | 24 | 52.01 | 52, 53, 50, 54 |
| Fe | 26 | 55.84 | 56, 54, 57, 58 |
| Ni | 28 | 58.69 | 58, 60, 62, 61, 64 |
| Cu | 29 | 63.57 | 63, 65 |
| Zn | 30 | 65.38 | 64, 66, 68, 67, 70 |
| Ag | 47 | 107.880 | 107, 109 |
| Cd | 48 | 112.41 | 114, 112, 111, 110, 113, 116. See page 157. |
| Sn | 50 | 118.70 | 120, 118, 116, 119, 117, 124, 122, 112, 114, 115 |
| Sb | 51 | 121.76 | 121, 123 |
| Hg | 80 | 200.61 | 202, 200, 199, 201, 198, 204, 196 |
| Pb | 82 | 207.22 | 208, 206, 207, 204 |
| Bi | 83 | 209.00 | 209 |

mixture containing $^{235}U$ and other uranium isotopes; by the use of this sample, $^{235}U$ was demonstrated as the source of nuclear energy (257) during the splitting of uranium by slow neutrons (Fig. 96, *c*).

Diffusion methods, too, have long been employed. The rate of diffusion of a molecule is inversely proportional to its molecular weight. Harkins, in 1921–6, by diffusion of HCl (Cl = 35.457) through porous membranes was able to obtain two hydrogen chloride fractions: in one the chlorine had a weight of 35.418, in the other, 35.515. Within the past decade diffusion of methane, $CH_4$, at very low pressures, employing a battery of fifty Langmuir pumps (368) has led to the concentration of the heavy carbon isotope, $^{13}C$, to a mixture containing 50% $^{13}CH_4$ (Capron and de Hemptinne, 1937). Unfortunately the operating pressures are too low and the actual yields therefore too small to enable large scale production of heavy isotopes by this method.

* *Berichte Deutschen Chemischen Gesellschaft* 71, 8–14, 1938.

Methods involving evaporation and distillation have not been too successful, although employed to some extent during 1920–30 in concentrating isotopes of mercury, chlorine, and zinc; and since 1930 to a small extent in concentrating $^{18}O$, by the evaporation of water, and of $^{15}N$ by the distillation of ammonia.

The electrolytic method has been most successful in concentrating deuterium, as is described in detail in Section 52.

An interesting method depending upon thermal diffusion has been devised by Clusius (1938), and studied by H. S. Taylor at Princeton, and Keith Brewer at the Bureau of Soil Chemistry in Washington. A pipe one to several inches in diameter contains the mixture of gases to be separated and, in the middle, a coaxial wire or small tube heated to dull red heat. Thermal currents produce an upward flow of gas in the vicinity of the hot wire, and a downward flow of gas at the inner surface of the cold pipe. After convection and diffusion have continued for minutes or hours, depending upon the length of the pipe (1 to 30 meters) and the gaseous species, a mixture relatively richer in the heavier isotope may be withdrawn from the lower end of the pipe; the upper end contains proportionately more of the lighter isotope. This method has been employed quite extensively in the concentration of heavy isotopes of chlorine, neon, carbon (as $CH_4$ or $CO_2$), and argon.

Since 1938 Urey has met with considerable success in preparing heavy isotopes by so-called **exchange reactions** taking place between gases rising in long columns against a descending stream of solution containing the proper ions:

$$H^{12}CN + (^{13}CN)^{-1} \rightleftarrows H^{13}CN + (^{12}CN)^{-1}$$

$$\underset{\substack{\text{gas}\\ \text{in}}}{^{12}CO_2} + \underset{\substack{\text{ions in}\\ \text{solution}}}{(H^{13}CO_3)^{-1}} \rightleftarrows \underset{\substack{\text{gas}\\ \text{out}}}{^{13}CO_2} + (H^{12}CO_3)^{-1}$$

The point of equilibrium is not always the same for two isotopes of the same element, so that in the cases cited above more of the heavy isotope is found in the gas which issues from the top of the column. Urey has successfully concentrated many grams each of the heavy isotopes of N, C, K and S by this method.

**245. Isotopes as Indicators.**—By the use of foods tagged with heavy isotopes, the biochemist may trace their course through the body. Thus D atoms may be substituted for some of the hydrogen atoms in beef fat, $(C_{17}H_{35}COO)_3C_3H_5$. By this method it was shown that fat is not stored for long periods of time; for $D_2O$ appeared in the urine in a few hours, all of the deuterium being thus accounted for within two weeks. Butter fat, on the other hand, was eliminated within nine hours from the time it was eaten.

The assimilation of sugars, too, has lent itself to heavy-isotope research. By substituting deuterium for some of the hydrogen in ordinary cane sugar, $C_{12}H_{22}O_{11}$, feeding this deuterized sugar to animals, killing the animals shortly afterwards, and analyzing their organs, it was demonstrated that sugar was first transformed into fat, which then burned within an hour.

Research of this sort is in its infancy, and the recent success in preparing heavy isotopes will soon lead to important biological discoveries. The heavy nitrogen isotope, for example, will reveal the fate of proteins in the body, inasmuch as the group $-NH_2$ is present in all proteins. On the other hand, $^{18}O$ cannot be successfully employed since molecules containing it undergo an exchange upon coming in contact with compounds containing $^{16}O$.

In chemical as well as biochemical fields these heavy isotopes are valuable tools.

Thus the rate of exchange between molecular hydrogen and the hydrogen atoms in methane, $CH_4$, can only be measured by mixing deuterium with methane:

$$CH_4 + D_2 \rightarrow CH_3D + HD,$$

and analyzing the products for $CH_3D$ and HD.

Again, suppose that the hydrogen atoms in only a certain portion of a large molecule undergo reaction. The chemist can ascertain which portion reacts by substituting deuterium for hydrogen in restricted parts of the molecule, and testing the reaction products for deuterium.

The rate of reaction in gases usually depends both upon the number of collisions between reacting species and the probability of reaction at the moment of collision. Without affecting the latter materially, the former factor may be considerably altered by substituting deuterium for hydrogen, since (84) velocity $H_2$ : velocity $D_2$ : : $\sqrt{4} : \sqrt{2}$. Such a change in velocity may drastically alter the course or rate of reaction, and indicate the reaction mechanism.

Radioactive isotopes are discussed in Section 254.

## C. RADIOACTIVITY

**246. Historical.**—The discovery of radium is one of the most important and brilliant contributions in the history of the world, for it has created a new science, namely, **radioactivity.**

In 1896 the French physicist, H. Becquerel, discovered that minerals containing uranium gave off rays which were capable of (1) *penetrating black paper and affecting the photographic plate;* (2) *producing fluorescence in certain substances* (zinc sulfide and barium platinocyanide); (3) *"ionizing" air and other gases and discharging an electroscope* (Fig. 97); and (4) *passing through plates of metal* (Fig. 99). These rays were called **"Becquerel rays"**; they are similar to X-rays in many of their properties. **Roentgen** had invented the X-ray tube only the year before (1895). About two years later, it was also discovered that thorium and its compounds

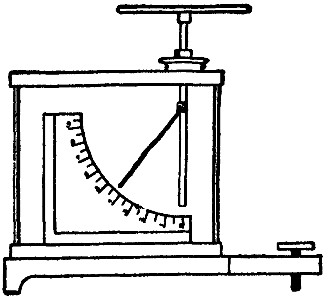


FIG. 97. An electroscope. The extended gold foil is discharged by radioactive rays.

possess properties similar to those of uranium and its compounds, and the name "radioactivity" was applied to these extraordinary properties.

Soon after the discovery of this new radiation, Madame Curie, working in conjunction with her husband, Professor Curie, of Paris, made the following generalization:

**Radioactivity is a property of the atom. It is not affected at all by the nature of the chemical combination in which the atom exists, nor by the physical conditions.**

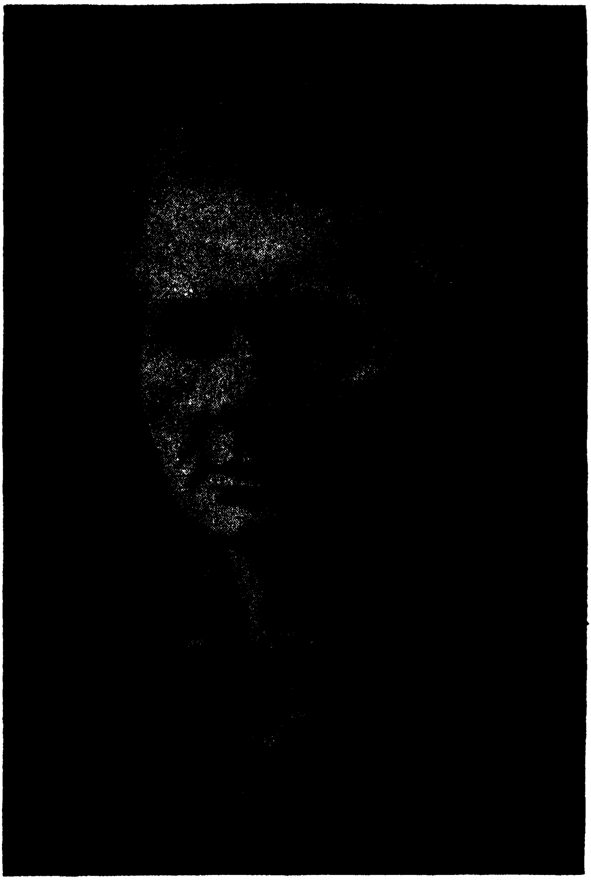
In 1897 the Curies worked on pitchblende residues [*Pitchblende* occurs in Bohemia; it contains the oxide, $U_3O_8$, as well as impurities] from which practically all the uranium had been extracted, and found that they were radioactive. They were led to suspect the presence of a new element in pitchblende more radioactive than uranium; indeed, they soon discovered a radio-element which was named **polonium** (Po—atomic number 84). It was found associated in small quantity with the bismuth extracted from the pitchblende.

Something like a ton of the residues was separated into different components, and it was discovered that the barium sulfate obtained was quite radioactive. By treating the barium sulfate, a small quantity of a new compound was prepared which was at least 1,000,000 times as active as uranium. The compound was radium bromide. They termed the new element, which was very radioactive, **radium**. The spectrum, general chemical relations, and atomic weight of the element showed it to be a member of the alkaline earth family.

Madame Curie succeeded in preparing pure radium chloride in 1902 and in isolating radium in 1910. Radium chloride was subjected to electrolysis, a mercury cathode being employed. The radium amalgam was placed in an iron boat, and the latter heated in a silica tube while a current of hydrogen under reduced pressure was being passed through. The mercury volatilized, leaving the radium behind as a white shining metal.

**247. Occurrence and Production of Radium.**—Uranium ejects particles from its nucleus spontaneously; it is therefore changing into some other element; this element, in turn, ejects another particle, and so on. The property of ejecting particles from the nucleus spontaneously is known as radioactivity. Some of the disintegration products from uranium are given in Table 52. Among them is radium.

**Radium is found, therefore, in all ores of uranium, and in no others.** Furthermore, the ratio between the radium present and the uranium is, in general, fairly constant, amounting to about 1 part of radium to 3,300,000 parts of uranium. This means that after uranium has been producing radium for a



MARIE SKLODOWSKA CURIE (1867–1934)

Born in Warsaw, where she received her first instruction from her father, a teacher; studied at the Sorbonne under Pierre Curie, whom she married; discovered *polonium* and (with her husband) *radium;* she stated that *radioactivity is a property of the atom;* awarded the Nobel Prize (1911); succeeded her husband as professor at the Sorbonne; head of the Radium Institute, Paris.

sufficient time the system comes to radioactive equilibrium, with about 3,300,000 times as much uranium as radium. This shows why the quantity of radium in existence is so small, and why it is so expensive to prepare it from uranium minerals. To illustrate, there are about 3 tons of uranium per gram of radium.

On May 25, 1921, Madame Curie was presented with a gram of radium at the National Museum in Washington. To secure this amount of the substance it was necessary to treat 500 tons of Colorado carnotite ore, containing 2 per cent of uranium. In 1 ton of pitchblende, containing 60 per cent of uranium, there is approximately 0.2 g. of radium.

In Europe, radium has been produced in considerable quantity from **pitchblende**, uranium oxide, $U_3O_8$. There are a number of impurities in the mineral, and the preparation of the bromide or the chloride from it is a complicated process.

Radium has been produced in greater quantities in the United States from **carnotite** ($K_2O, 2UO_3, V_2O_5, 3H_2O$), a light canary-yellow mineral, occurring chiefly in Colorado and Utah. This is a valuable ore, for it has been worked for uranium and vanadium as well as radium.

In 1922 discovery of a radium ore in the Katanga district of the **Belgium Congo** stopped production in the United States, for the African ore was much richer in radium than any other ores hitherto known. The ore was refined in Belgium.

Production of radium swung back to the Western Hemisphere in 1930. At that time a lone prospector, La Bine, searching for cobalt and silver ores within the **Arctic circle in the Canadian Northwest came upon an enormous deposit of pitchblende at Great Bear Lake.** The meteoric rise in radium production in Canada is reflected in the radium out-put since that time: 1933, 3 grams; 1935, 8½ g.; 1937, 24 g.; 1939, 108 g., the latter representing probable annual production. Since only 300 g., approximately three-quarters of a pound, of radium had been produced during the period 1900–1930, it can be seen that La Bine's discovery transferred the radium monopoly of the world to Canada. Simultaneously the price of radium tumbled: $125,000 per gram in 1918, $70,000 per gram in 1932, $25,000 per gram in 1941.

The Eldorado Radium Corporation, which handles this radium production, flies the ore, thousands of tons of it every year, southward several hundred miles; and then it is transported by boat the remainder of its 3500 mile journey to the refinery at Port Hope, near Toronto, where the radium is extracted from the ore by a process invented and directed by M. Pochon, one of Madame Curie's pupils.

**248. The Nature of the Radiations.**—Radioactive substances emit three principal types of radiation, namely, the *alpha* ($\alpha$), the *beta* ($\beta$), and the *gamma* ($\gamma$). The three types of 'rays' affect the photographic plate, cause certain fluorescent substances to glow, and 'ionize' the air and other gases. These effects, as well as the different types of fog tracks (242) obtained with these radiations, are used in the detection and measurement of the different radiations.

**($\alpha$) Alpha Particles.** These rays are positively charged atoms of helium ($He^{++}$), or helium atoms each minus two electrons, which move with approximately one-tenth of the velocity of light (30,000 kilometers per second). They can be detected by means of the Crookes **spinthariscope** (Greek, *spark* + *to view*). A minute quantity of a radium compound is placed in front of a screen covered with zinc sulfide (Fig. 98). When the helium particles strike the zinc sulfide, flashes of light are produced, which are magnified by means of a lens. By resting the eye in a dark room for 15 to 20 minutes, the flashes may be seen. The alpha rays are feebly penetrating, nearly all being stopped by a sheet of paper, or by a sheet of aluminum 0.1 mm. thick (Fig. 99). The alpha rays, being positively charged, are affected by a magnetic field, as shown in Fig. 100, but are deviated in the opposite sense to the beta rays. The deviation is slight, however, for the mass is great as compared with that of the beta rays. The alpha particle possesses a mass about four times that of the hydrogen atom.

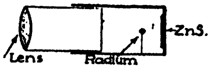


FIG. 98. The Crookes spinthariscope.

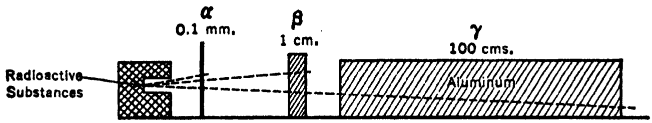


FIG. 99. Penetrability of radioactive rays through aluminum.

(β) **Beta Particles.** These rays are identical with cathode rays, *i.e.*, they are electrons, or free atoms of negative electricity. The velocity of beta particles varies in different cases, the maximum being nearly as great as that of light (300,000 kilometers per second). They have greater penetrating power than alpha particles, but are virtually stopped by a sheet of aluminum 1 cm. thick. These rays are greatly deviated by a magnetic field, and also ionize the air, producing fog-tracks which are fainter than those of the alpha rays. The mass of the electron is very small, being about 1/1836 of the hydrogen atom. See figures 95–100.

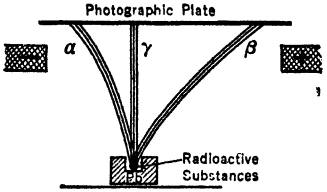


FIG. 100. Deflection of radioactive rays in a field.

(γ) **Gamma Rays.** These rays are very similar to X-rays, that is, light waves of exceedingly short wave length. Thus visible light has a wave length of 4000–8000 Ångstroms (1 Ångstrom unit = $10^{-8}$ cms.), but X-rays are only 10–100 Ångstroms long. These gamma rays have great penetrating power, being able to penetrate relatively thick layers of metals. They are not deviated by a magnetic field. The fog-tracks (242) of gamma rays show myriads of droplets which have condensed on ions produced by the gamma rays striking molecules of oxygen, nitrogen and other gases in the air (Fig. 96, *a*).

**249. The Displacement Law.**—It is evident that a heavy element such as radium, atomic weight 226, contains a huge number of particles within the nucleus. In a sense this leads to an unstable nucleus which tends to fly apart, ejecting the alpha, beta and gamma radiations. The loss of one of these particles has various effects.

**α, alpha particle.**—Loss of one of these particles decreases atomic weight 4 units, lowers atomic number 2 units; for the alpha particle weighs 4, and its charge is +2.

**β, beta particle.**—Loss of this electron has no effect upon the atomic weight of the parent atom, since the weight of an electron is negligible (1/1836). On the other hand its charge is −1; a loss of a minus charge from the nucleus increases its positive charge 1 unit; the atomic number increases by 1 unit.

**γ, gamma ray.**—Since the gamma ray has neither appreciable weight nor charge, no changes in atomic weight or atomic number occur whenever this radiation comes from the nucleus.

If during the above changes the charge on the nucleus is altered, the planetary system of the residual atom picks up electrons from, or loses them to, the atmosphere. This occurs shortly after the radioactive emission, and the atom thus remains neutral.

Examination of Table 52 and Fig. 101 showing the disintegration of Uranium into Lead, confirms the facts stated above as regards changes in atomic weight and number.

In passing from uranium to lead, eight alpha particles are ejected. This represents a loss in weight of 8 × 4 = 32 units; so that $^{238}U$ becomes $^{206}Pb$. Now ordinary lead, from non-radioactive sources, has an atomic weight of 207.22. In 1913, Soddy suggested that lead derived from minerals containing uranium might have a lower atomic weight. T. W. Richards determined the atomic weight of lead in a very pure specimen of uranio-lead from Norwegian cleveite and found it to be 206.08, a number in striking agreement with the theory of Rutherford. This atomic weight of lead has been confirmed by other investigators. According to Richards, ordinary lead has a density of 11.337, while that of uranio-lead is 11.273, a difference of 0.56 per cent.

RADIOACTIVE SERIES AND THE GROUP DISPLACEMENT LAW

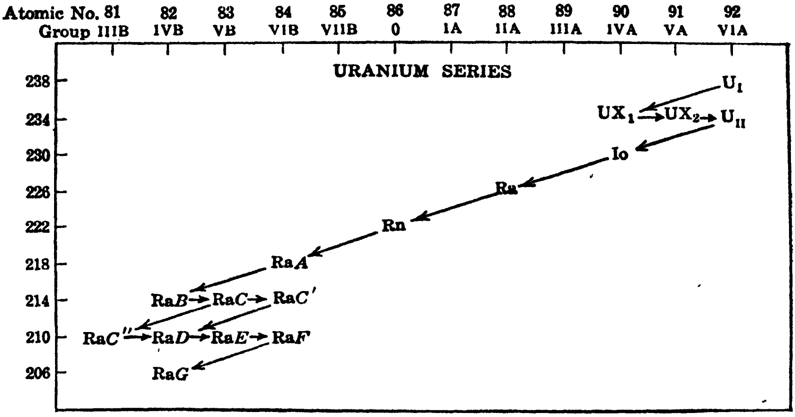


FIG. 101. The Uranium Series and the Displacement Law.

TABLE 52. THE URANIUM SERIES

| Element | At. Wt. | At. No. | Rays | Half-life Period |
|---|---|---|---|---|
| **Uranium-I** | **238.2** | **92** | $\alpha$ | **4.4 × $10^9$ years** |
| Uranium-$X_1$ | (234) | 90 | $\beta$ | 24.5 days |
| Uranium-$X_2$ | (234) | 91 | $\beta$ | 1.14 min. |
| Uranium-II | (234) | 92 | $\alpha$ | 3.4 × $10^5$ years |
| Ionium | (230) | 90 | $\alpha$ | 8.3 × $10^4$ years |
| **Radium** | **226.05** | **88** | $\alpha$ | **1590 years** |
| Radon (Gaseous emanation) | 222 | 86 | $\alpha$ | 3.85 days |
| Radium-A | (218) | 84 | $\alpha$ | 3.05 min. |
| Radium-B | (214) | 82 | $\beta$ | 26.8 min. |
| Radium-C | (214) | 83 | $\beta$ and $\alpha$ | 19.7 min. |
| 99.97% 0.03% | | | | |
| Radium-C′ | (214) | 84 | $\alpha$ | $10^{-6}$ seconds |
| Radium-C″ | (210) | 81 | $\beta$ | 1.32 min. |
| Radium-D | (210) | 82 | $\beta$ | 22 years |
| Radium-E | (210) | 83 | $\beta$ | 5.0 days |
| Radium-F **(Polonium)** | (210) | 84 | $\alpha$ | 140 days |
| **Radium-G (Lead)** | **206** | **82** | **(not radio-active)** | — |

**250. Half-life Period.**—In the last column of Table 52 there is listed the time which it takes for 50% of a given amount of each radioactive element to disintegrate. That is, the ejection of these nuclear particles runs exactly on schedule; for although it is spontaneous, it is also as regular as clockwork. Thus a gram of uranium will have half-disintegrated after 4.4 billion years; while a gram of RaC′ will be half gone in a millionth of a second. Stated another way, this means that the number of particles emitted per second by a gram of RaC′ will be overwhelmingly greater than the number emitted by a gram of uranium; that is why the uranium lasts longer.

Radon, the radioactive gas, is excellent for studying the chemical effects of alpha particles since it emits an intense radiation of them. On the other hand it has a half-life of only 3.85 days, so that its usefulness is soon ended, in fact only a few days after it has been collected. This is one reason why **radium** plays so important a role among all of these 15 radioactive substances; for its half-life, 1590 years, is long enough for radium to be regarded as a practically permanent source of radioactivity, but, at the same time, short enough to render it a highly active and concentrated source.

Since the disintegration is proceeding at a perfectly definite rate, determination of the U, He, Pb, etc. ratios will indicate how long the sample has been disintegrating. Thus one gram of uranium gives off helium at the rate of 1 cc. in 16,000,000 years. Samples of the mineral fergusonite contain 26 cc. of accumulated helium gas per gram of uranium; hence it is concluded that the samples of this mineral are at least 416,000,000 years old. Some of the helium may leak out, since it is a gas. There are also other

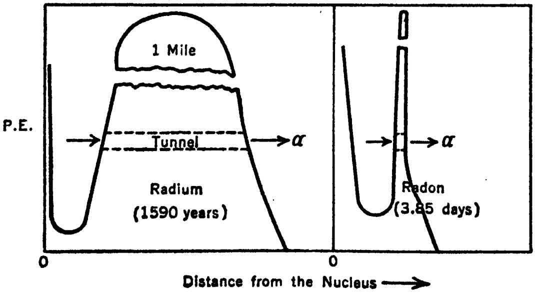


FIG. 102. Radioactive decay and leak through a potential energy barrier (Gurney and Condon).

complications. Radioactivity indicates that the earth is at least 1,500,000,000 years old.

It is of interest to consider radioactive decay in terms of potential energy curves, and attribute rapid decay to low energy of activation, just as those chemical reactions which occur most rapidly have the lowest potential energy humps (Section 191, Fig. 85). When such curves are constructed, it is seen that the heights are far too great for any measureable decay to occur. Gurney and Condon explained the decay as a "leak through the barrier," those elements decaying most rapidly which had the narrowest humps (Fig. 102). By their assumption, they were able to calculate the half-life period for all of the radioactive elements. This is another achievement of mathematics in the field of chemistry.

**251. Other Disintegration Series.**—Besides the uranium disintegration series, there are two other similar radioactivity series. The **actinium series** begins with protactinium, at. wt. 231, at. no. 91, and transmutes via 9 other radioactive elements to the end-product actinium-D, at. wt. 207, at. no. 82. The **thorium series** passes from thorium (at. wt. 232.12, at. no. 90) to thorium-D (at. wt. 208, at. no. 82) which is an isotope of lead. It includes the two elements with extreme half-life periods: thorium, half-life 13.4 billion years, and thorium C′, half-life about ten-trillionths of a second.

Besides these three series, which contain 36 radioactive elements and 3 end-products which are not radioactive, several other radioactive elements exist in nature, *viz.* $^{40}K$. Recently a large number of radioactive elements have been produced artificially (257).

**252. Physical Properties of Radium.**—Radium is a silvery metal which melts at 700° and loses its luster in the air. It is similar to barium, although its compounds are less soluble in water. It is more reactive than barium and less reactive than sodium. Radium compounds impart a carmine color to the Bunsen flame.

When particles are ejected from the radium nucleus tremendous heat is evolved. As a result, the atmosphere in the vicinity of a radium compound is about 4° above room temperature. One gram of radium evolves 134 calories per hour, heat more than enough to raise its own weight in water from the freezing point to the boiling point; while in ten years the energy set free by one gram of radium equals that developed in the burning of over a thousand grams of coal.

**253. Chemical Effects of Radium Radiations.**—The rays emitted by radium, radium compounds, or other radioactive substances have been extensively investigated by S. C. Lind, in this country. The chemical effects of alpha particles are investigated by a special technique. Radon gas is confined in a bulb the size of a pin-head, the glass walls of which are so thin that the ejected alpha particles pass through them into an outer bulb containing the gases to be acted upon by the rays. The results are not very different from ordinary photochemical reactions. Thus chlorine can be made to combine with hydrogen; oxygen with carbon monoxide; nitrogen with hydrogen. In many of these reactions it is possible first to calculate the number of ions (ion-pairs) produced by the alpha particles; then this value is applied in ascertaining **the number of molecules reacting per ion-pair produced.** By this study it is seen chain reactions (205) as well as normal reactions can be initiated by alpha particles.

The rays decompose water. It is therefore dangerous to seal up radium or other highly radioactive substances, either in solution or in an imperfectly dried condition for indefinite periods, for the gases formed might burst the containing vessel. The radiations also have a coloring action on common glass and on many gems and minerals. Ordinary glass is usually colored violet or purple, but sometimes brown. The rays produce fluorescence in many substances: *e.g.*, zinc sulfide, barium platinocyanide, and the diamond. Again, they sterilize seeds and destroy microorganisms.

Not only is radium sold to hospitals and physicians, but it has been extensively used in the manufacture of luminous enamels or paints, a minute quantity of a radium salt being mixed with zinc sulfide. The principle involved is the same as in the spinthariscope; that is, zinc sulfide is bombarded by helium or alpha particles, light being produced. In the course of time the zinc sulfide is worn out, but the radium compound may be recovered and used again. **Mesothorium**, a disintegration product of thorium, is luminous in the dark. It is now used on the faces of watches. Its average life is nearly 10 years and its half-value period is 6.7 years.

**Radium is employed in the treatment of cancer and allied diseases.** It is announced that it is a cure for certain types of cancer, being of great value in the treatment of skin, lip, tongue, and tonsil cancers; it is also an important aid in surgery, and serves as a palliative in certain incurable diseases. Radium has been applied with success to chronic infected wounds, and has aided in the treatment of scars. The alpha rays are feebly penetrating, and are but little used. Beta radiation is always employed in conjunction with gamma radiation. Beta radiation is used for superficial conditions, and the gamma radiation in this case may probably be ignored. Gamma radiation is employed when deep penetration is required. One of the chief objects in the employment of radium is to get the effect of the deeply penetrating gamma rays. In the application of radium it must be borne in mind that its rays may produce sores, for they have a tendency to kill the cells of the skin. Radium is continually producing emanation (radon, Rn), which may be substituted for radium in the treatment of disease. The emanation is pumped off from time to time, collected in tiny glass tubes, and then inserted in the flesh near the cancer or similar growth. The emanation breaks down, producing the "rays," which act on the diseased tissue.

Since 1936 **many hospitals have installed very high-voltage X-ray machines** as a substitute for radio-therapy in certain treatments. For example, the 1,250,000-volt apparatus erected at the Harvard Medical School in 1939 supplies greater gamma intensity than all the radium in use in the world today; and similar machines are being installed in other hospitals.

**254. Radioactive Indicators.**—Thorium, bismuth, lead and thallium have both radioactive and stable (non-radioactive) isotopes (243). In addition, radioactive isotopes of about eighty other elements have been made (257). Now the detection of the radioactive rays is billions of times more delicate than any chemical methods yet devised. The addition of traces of a radioactive element to one of its stable isotopes therefore tags that isotope just as deuterium tags hydrogen compounds (73). This enables the chemist to make measurements at concentrations vastly smaller than any chemical analysis would detect.

For example, by the use of radioactive lead as an indicator, *the solubilities of a lead salt* can be accurately determined when there is as little as one billionth of a gram of salt per cc. of solution. *The inter-diffusion of molecules* in a bar of lead can be followed. For this purpose a section of radioactive lead is melted to the end of a bar of ordinary lead; and from day to day the advance of the radioactive atoms can be measured by the rays which they emit. Again, *the active surfaces of powdered crystals may be studied.* Powdered $PbCl_2$, $PbCrO_4$ or $PbSO_4$ absorb ions of lead on its surface. Placed in solutions of lead salts containing a trace of radioactive lead as indicator, some radioactive atoms as well are adsorbed. From the intensity of their radiation the number of atoms adsorbed on the surface of the powder can be calculated. Further, a comparison of this surface with the quantity of dyes adsorbed on the same powder indicates that the dyes form an adsorption layer only one molecule thick. Such data have obvious implications in interpreting catalytic reactions at surfaces.

After 1934 the preparation of many new radioactive elements (257) considerably extended the scope of radioactive indicator work. Diffusion of radioactive gold was measured, as described for lead in the preceding paragraph. HBr containing radioactive bromine was used to show that the following exchange takes place in a few minutes at room temperature:

$$HBr_{r.a.} + Br_2 \rightarrow HBr + Br \cdot Br_{r.a.}.$$

A good deal has been accomplished with **radioactive indicators in biochemistry**. A great mobility of salts within the different parts of plants and animals has been demonstrated. For example, when a plant containing stable lead salts in its leaves was placed in a soil containing radioactive lead, part of the stable isotope in the leaves was replaced by radioactive lead. Again, phosphorus in the bones is being continuously replaced by new phosphorus atoms, for when a diet of radioactive phosphates was fed to animals, the radioactive isotope was detected in the bones. Radioactive phosphate diets were fed to chicks, which were killed for analysis some days after the feeding. The phosphorus appeared in the brain and bone marrow. The rate of absorption of sodium chloride from the digestive tract by the blood stream was measured by having the patient drink radioactive brine while holding a ray counter in his hand. By feeding radioactive potassium chloride to rats, they were found to absorb potassium within half an hour; the potassium was retained chiefly by the muscles and soft tissue. Radioactive iodine was shown to be selectively absorbed by the thyroid gland in rabbits; twelve other tissues examined contained no iodine. These and a host of other biological discoveries have been made possible by the use of radioactive indicators.

## MODERN ALCHEMY

**255. Transmutation upon Bombardment with Alpha Particles.**—Having studied the transmutation of some elements by the spontaneous disintegration of the nucleus, the student may wonder whether such transmutations may be achieved in the laboratory by artificial means. This has been one of the outstanding achievements of the past two decades, particularly since 1934.

In 1919 Rutherford noticed that when a swiftly moving alpha particle collided with nitrogen gas the following transmutation occurred:

$$^{4}_{2}\mathrm{He} + {}^{14}_{7}\mathrm{N} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H},$$

and that other lighter elements up to calcium were similarly affected, with the exception of helium, carbon and oxygen. The dream of the alchemist of the Middle Ages, transmutation, at last had come to pass.

Bothe and Becker (1930) discovered a second type of transmutation which was explained by Chadwick (1932) as leading to the production of a hitherto undiscovered particle, the *neutron:*

$$^{4}_{2}\mathrm{He} + {}^{9}_{4}\mathrm{Be} \rightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}n,$$

and neutrons were similarly produced when aluminum, arsenic, bromine, chromium, cobalt, copper, and nickel were bombarded with swiftly moving alpha particles.

Still another transmutation among these pioneer attempts led to the production of an artificial radioactive element. This was accomplished by the daughter of Madame Curie, Irene, and her husband, Joliot, in 1933, for which they received a Nobel Prize. The reaction was

$$^{4}_{2}\mathrm{He} + {}^{10}_{5}\mathrm{B} \rightarrow {}^{13}_{7}\mathrm{N} + {}^{1}_{0}n,$$

but the $^{13}_{7}\mathrm{N}$ was radioactive, and disintegrated into $^{13}_{6}\mathrm{C}$ in a few seconds:

$$^{13}_{7}\mathrm{N} \rightarrow {}^{13}_{6}\mathrm{C} + \text{a positron.}$$

**256. The Cyclotron.**—For artificial transmutation to be achieved, a missile must be hurled with tremendous force against the nucleus of the atom. As we have seen in the preceding section, alpha particles which are moving swiftly enough are successful.

In 1933 E. O. Lawrence of California constructed a machine, **the cyclotron,** which will accelerate particles such as $H^+$, $D^+$, and $He^{++}$ sufficiently to use them as missiles in effecting transmutations. By the use of this machine over a thousand transmutations were accomplished between 1935 and 1941. In principle the cyclotron imparts a succession of 60,000 volt impulses to these charged particles until it has built up an effective energy of some 50,000,000 electron-volts.[1] At this point the particle is hurled against the target where the transmutation is to occur, often in a C. T. R. Wilson cloud chamber where a fog-track of the collision reveals the resulting transmutation (**242**).

The apparatus (Fig. 103) consists of two flat semicircular boxes *A* and *B* separated by a small gap. A charged particle ($H^+$, $D^+$, $He^{++}$) which is to be used as the missile emerges from the tube at point *a* in the slit between the two segments. A potential difference of 60,000 volts is applied to the two segments, and the positively charged particle moves rapidly towards the negative segment to point *b*. Within the segment it describes a curved path due to a powerful magnetic field imposed upon it by a heavy magnet above and below the segments. These magnets, weighing hundreds of tons, are usually the part of the apparatus seen by the layman in pictures of the cyclotron. After the missile reaches *c*, an oscillator controlling the charge on the segments reverses the charge so that the swiftly moving particle is now attracted and pushed across the gap again, to point *d*; this time with double the energy, *i.e.*, 120,000 electron-volts. Continuing in its curved path to *e*, it again finds the charge on the segments reversed, and is again forced across the gap, reaching *f* with a velocity of 180,000 electron-volts. This process con-

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[1] One electron-volt is the energy acquired by a particle carrying a charge of 1*e*, when it falls freely through a potential difference of 1 volt (1 electron-volt = $1.6 \times 10^{-12}$ ergs).

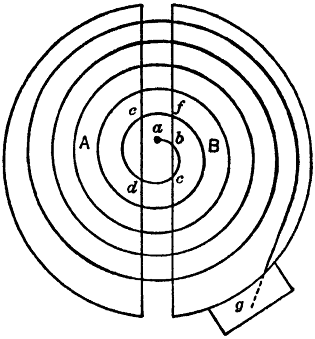
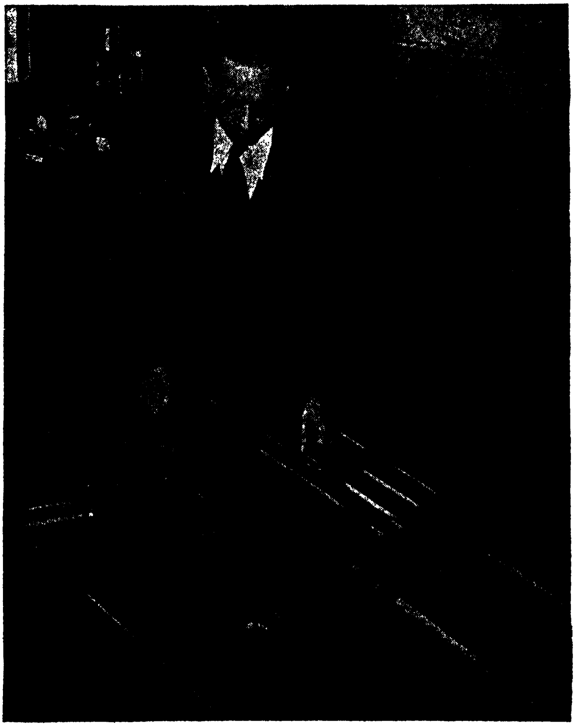


FIG. 103. Simplified scheme of the cyclotron.



*World Wide Photos, Inc.*
*Courtesy J. J. Livingood.*

**FIG. 104. The cyclotron dees.**

tinues, and after many revolutions the particle has acquired an energy of several million electron-volts. At this point it ploughs into the target $g$ where transmutation occurs; this is usually photographed as a fog-track, for the quantity of material transmuted is usually so tiny that it cannot be detected by chemical analysis.

In 1941 Professor Lawrence, who had raised a million and a half dollars for a new machine, had completed his plans to construct a 5000-ton cyclotron with which he hoped to attain energies of 100,000,000 electron-volt alpha particles, and 50,000,000 electron-volt deuterons.

**Neutrons** which, because they are lacking in charge, cannot be accelerated in the cyclotron, may be obtained as secondary products. In this case $He^{++}$, accelerated in the cyclotron, is shot against $^{9}_{4}Be$, producing fast neutrons by equation 2, Section 255. Since slow neutrons are often desired, they are retarded by passage through water or paraffin wax.

In addition to the cyclotron, Van der Graaf and others have devised machines for generating several million volts similarly to accelerate missiles so that they will penetrate the nuclei of targets and cause transmutations.

**257. Some Artificial Transmutations.**—It is possible to present only a brief survey of the thousand transmutations accomplished between 1935 and 1941.

Bombardment with **neutrons** is successful in making radioactive nearly all of the known elements. Emitted at the same time is (*a*) a proton or (*b*) an alpha particle or (*c*) two neutrons, or (*d*) gamma radiation. For example:

$$^{1}_{0}n + ^{27}_{13}\mathrm{Al} \rightarrow ^{27}_{12}\mathrm{Mg} + ^{1}_{1}\mathrm{H}.$$

Bombardment with **protons** yields (*a*) alpha particles or (*b*) deuterons or (*c*) neutrons or (*d*) gamma rays:

$$^{1}_{1}\mathrm{H} + ^{9}_{4}\mathrm{Be} \rightarrow ^{6}_{3}\mathrm{Li} + ^{4}_{2}\mathrm{He}.$$

Bombardment with **deuterons** produces (*a*) protons or (*b*) alpha particles or (*c*) neutrons, or alpha particles with either (*d*) protons or (*e*) neutrons:

$$^{2}_{1}\mathrm{D} + ^{31}_{15}\mathrm{P} \rightarrow ^{32}_{15}\mathrm{P} + ^{1}_{1}\mathrm{H}.$$

In some cases very short **gamma radiation** has also been shown to produce an unstable, radioactive nucleus by ejecting a neutron.

A most interesting result was the artificial production from bismuth of one of the elements in the uranium disintegration series. J. Livingood (Fig. 104) working in Lawrence's laboratory in 1936 discovered the transmutation

$$^{209}_{83}\mathrm{Bi} + ^{2}_{1}\mathrm{D} \rightarrow ^{210}_{83}\mathrm{RaE} + ^{1}_{1}\mathrm{H}.$$

The RaE produced by this method from bismuth is identical with RaE in the uranium series in Table 52. Its half-life period, like natural radium-E, was 5.0 days, and its beta radiation was the same as the natural product.

The chief source of artificial radioactive material for biological research, before the advent of high voltage generators and cyclotrons, was from slow neutrons (equation bottom of page 306). The neutrons, after being slowed down by passage through water or paraffin wax, produce changes such as the following:

$$\underset{\text{slow}}{^{1}_{0}n} + ^{23}_{11}\mathrm{Na} \rightarrow \underset{\text{radioactive}}{^{24}_{11}\mathrm{Na}} + \text{gamma ray}$$

$$^{24}_{11}\mathrm{Na} \rightarrow ^{24}_{12}\mathrm{Mg} + \underset{\beta\text{-ray}}{^{0}_{-1}e}$$

### NUCLEAR ENERGY

**258. Origin of the Sun's Energy (Bethe).**—Changes within the nucleus are attended by tremendous energy changes, millions of times greater than the heats of reactions associated with ordinary chemical reactions. These latter, it will be recalled, involve shifts in the planetary electrons, in contrast with the nuclear changes we are about to discuss.

Taking advantage of the transmutations revealed by cyclotron studies, Bethe (Cornell, 1939) proposed a mechanism which gave the production of energy in the sun at its internal temperature of twenty million degrees. Bethe reproduced these reactions in the laboratory. The steps involved

$$\begin{array}{ll}
(a) & \mathrm{H} + {}^{12}\mathrm{C} \rightarrow {}^{13}\mathrm{N} \\
(b) & \qquad {}^{13}\mathrm{N} \rightarrow {}^{13}\mathrm{C} + e^{+} \text{ (a positron)} \\
(c) & \mathrm{H} + {}^{13}\mathrm{C} \rightarrow {}^{14}\mathrm{N} \\
(d) & \mathrm{H} + {}^{14}\mathrm{N} \rightarrow {}^{15}\mathrm{O} \\
(e) & \qquad {}^{15}\mathrm{O} \rightarrow {}^{15}\mathrm{N} + e^{+} \\
(f) & \mathrm{H} + {}^{15}\mathrm{N} \rightarrow {}^{12}\mathrm{C} + {}^{4}\mathrm{He} \\
\hline
\text{Total} & 4\mathrm{H} + {}^{12}\mathrm{C} \rightarrow {}^{12}\mathrm{C} + 2e^{+} + {}^{4}\mathrm{He}
\end{array}$$

It will be observed that carbon plays the role of catalyst, being regenerated at the end of the sequence; and that four hydrogen atoms, weight 4 × 1.0080 = 4.0320 g., react to give one helium atom, weight 4.0039. A total of 0.0281 g. has disappeared; matter is transformed into energy, and Bethe's calculations show that this energy is sufficient to account for the temperature of the sun.

Bethe extended his calculations to the mass-luminosity relations observed in other stars.

**259. Tapping Nuclear Energy.**—The student may well wonder if such enormous quantities of nuclear energy may someday be made available to mankind by transmutations in the laboratory; and, if accomplished, whether the scientist will be able to harness this force.

In December, 1938, for the first time in history this nuclear energy was tapped. Meitner and Hahn in Berlin were repeating experiments by Fermi, Italian Nobel Laureate who believed that he had obtained elements with atomic numbers above 92 upon bombarding uranium with neutrons.[1] They showed that, instead, the uranium atom had split approximately in half, forming barium, krypton, neutrons and the enormous energy of 175,000,000 electron-volts.

This was quickly confirmed (January 1939) in Bohr's laboratory in Copenhagen, and in a number of universities in the United States. The splitter particles were not always barium: caesium, iodine, rubidium, strontium, and others were also reported, but in each case a yield of tremendous nuclear energy was obtained.

A few months later Bohr and J. Wheeler at Princeton suggested that, on theoretical grounds, the uranium isotope $^{235}$U was responsible for the change. Nier at Minnesota concentrated this isotope in his spectrograph (**113**) from natural uranium which contains 1$^{239}$U, 1/140 $^{235}$U, and 1/17,000 $^{234}$U; and scientists at Columbia University using his $^{235}$U confirmed the Bohr-Wheeler suggestion.

The energy liberated by this process is enormous. One pound of U$^{235}$ is equivalent to 5,000,000 pounds of coal, 3,000,000 pounds of gasoline, or 15,000 tons of T.N.T. explosive. A few pounds of it would drive an ocean liner for months.

Since the process involves a capture of the neutron by the $^{235}$U nucleus, only slow neutrons are effective. The energy can be caught in water surrounding the $^{235}$U. Also, since the process releases one or more neutrons, once started it might become self-propagating.

A wave of speculation swept the civilized world with the thought that the energy in the nucleus was at last made available to mankind. But, to quote Kingdon of the General Electric:

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[1] Some of Fermi's work has been substantiated. In 1940 McMillan and Abelson obtained elements number 93, 94 and 95 by the Fermi reactions.

"Applications will involve problems of proper control of the power, and protection against the tremendous neutron and X-ray radiations which will accompany it. It may be that the use of these radiations in therapy will be one of the most important applications. But detailed discussion of these questions is premature until further progress has been made in the separation of large quantities of $^{235}U$."

Since Nier's spectrograph yields only 0.001 milligrams of $^{235}U$ per day, a pound every 12 million years, success is still very much in the offing.

The nuclei of protoactinium and thorium, like $^{235}U$, have since been shown to release nuclear energies under similar conditions.

## QUESTION REVIEW

### PHENOMENA CONNECTED WITH THE NUCLEUS

I. NUCLEAR STRUCTURE. **Electron (238). Wide angle deflection (239). Ejected particles (240–241). Fog tracks (242).**

1. Describe two different lines of evidence of the existence of the electron.
2. Give the details of the Millikan oil-drop method for determining the charge, *e*, on an electron.
3. Describe the experimental evidence which led Rutherford to propose a nuclear structure for the atom. About how empty is an atom?
4. Diagram the three oxygen isotopes.
5. Describe the type of fog-track which would be obtained in a magnetic field from an electron, from an alpha particle, from a positron, and from a neutron.
6. Explain how transmutations are revealed by their fog-tracks.

II. ISOTOPES. **(243). Heavy isotopes (244). Indicators (245).**

7. What are the isotopes of hydrogen, carbon, nitrogen, and oxygen (refer to the table of isotopes)?

8. What heavy isotope is used, and what new biological processes are revealed, in the assimilation of fats and sugar in the body? What isotope is now used for studying proteins?

## III. RADIOACTIVITY.

**a. Historical (246). b. Occurrence (247).**

9. Who discovered radioactivity? What part in its history was played by the Curies?
10. Which countries have been the chief producers of radium? Who holds the monopoly today?

**c. The radiations (248). Displacement law (249). Half-life (250).**

11. Describe the properties of alpha, beta and gamma rays as regards (*a*) penetrability, (*b*) velocity, (*c*) ionizing properties, (*d*) fog tracks, (*e*) deviation in a magnetic field.
12. Complete the following table, keeping in mind the changes in atomic weight and atomic number whenever alpha or beta particles are ejected.

| Element | Atomic Weight | | Atomic Number | | Particle Ejected (Alpha or Beta?) | |
|---|---|---|---|---|---|---|
| Thorium | 232 | | 90 | | ? | |
| Meso-Thorium-I | 228 | | ? | | ? | |
| Meso-Thorium-II | ? | | 89 | | ? | |
| Radio Thorium | ? | | ? | | alpha | |
| Thorium-X | ? | | ? | | alpha | |
| Thoron | 220 | | ? | | alpha | |
| Thorium-A | ? | | 84 | | ? | |
| Thorium-B | ? | | 82 | | beta | |
| Thorium-C | ? | | ? | | from C giving C′ ? | from C giving C″ ? |
| Thorium C′ and C″ (65%) (35%) | Of C′<br>212 | Of C″<br>208 | Of C′<br>? | Of C″<br>? | from C′ giving D ? | from C″ giving D ? |
| Thorium D (same end product from C′ and C″) | ? | | ? | | | |

13. In the foregoing table, which elements are isotopes? Which elements in this table are isotopes of elements in the Uranium series, table 52?
14. What are the advantages and disadvantages in the use of radon (radioactive gas) in studying the chemical effects of alpha particles?
15. Why is radium considered so much more important than the thirty-six other similarly radioactive elements?
16. Show how radium may be used to determine the age of the earth.

**d. Other disintegration series (251).**

**e. Properties of radium (252–253). Use as indicator (254).**

17. State the physical properties of radium.
18. Describe the apparatus used in studying the chemical effects of alpha particles. What are some of the results obtained?
19. Explain the therapeutic use of radium. What is replacing the use of radium in hospitals?
20. Describe several researches involving the use of radioactive elements as indicators.

IV. MODERN ALCHEMY. **α-particles (255). Cyclotron (256–257).**

21. Describe the transmutations effected by alpha particles in the experiments by (*a*) Rutherford, 1919, (*b*) Bothe and Becker, 1930, (*c*) Curie-Jolliot, 1934.
22. What is the principle of the cyclotron? Explain its operation in detail.
23. Give equations showing two artificial transmutations made possible by the use of the cyclotron.

V. NUCLEAR ENERGY. **Sun (Bethe) (258). Uranium (259).**

24. Without giving the individual steps, give an equation showing the over-all reaction which produces the energy which keeps the sun hot.
25. Give an historical outline of the discoveries which have led up to the tapping of nuclear energy.

**Reading References:** Articles number 55, 72, 74, 121, 212, 328, 406 and 413 in the Appendix.

# CHAPTER XX

# ATOMIC STRUCTURE

## PART II. PHENOMENA CONNECTED WITH THE PLANETARY ELECTRONS

**260. Principle Quantum Number, *n*.**—The arrangement of electrons in shells outside of the nucleus has already been discussed (55). This picture was developed by Niels Bohr, in 1913, following Rutherford's concept of the nuclear atom (239).

In his calculations Bohr assumed that the electrons are assigned to definite orbits, numbered 1, 2, 3, and so forth. These are called the **principle quantum numbers.** $n = 1$, for example, represents the orbit closest to the nucleus. Bohr assumed that the energy content $E_n$ of each orbit [1] was equal to $k/n^2$; that is, orbit 1 would have $E_1 = k/1$, orbit 2 would have $E_2 = k/4$, orbit 3 would have $E_3 = k/9$.

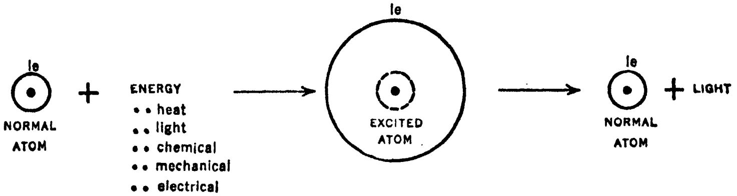

FIG. 105. Origin of the spectrum.

Einstein in 1905 had stated that whenever an electron changes to a level of lesser energy content the difference in energy is released solely as light. (Fig. 105.) Now if each orbit has a definite quantity of energy, $k/n^2$, a change of an electron from an outer orbit to one closer to the nucleus would result in the release of a definite quantity of energy. For example, a drop from orbit 3 to orbit 2 would be accompanied by the release of $E_2 - E_3 = (k/4) - (k/9)$ units of energy. Since this energy, released solely as light, is a definite unit of energy, it would correspond to one wave length of light, that is, to a single spectral line. A jump from orbit 3 to orbit 1 would give off more energy, $(k/1) - (k/9)$, so the light would be further towards the ultra-vio-

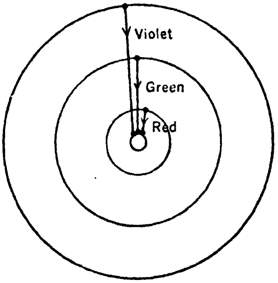

FIG. 106. Light released by electron jumps. The greater the jump, the nearer the ultraviolet end of the spectrum is the light emitted.

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[1] Students who have had atomic physics will recognize that $k$ is the Rydberg constant, $R$, (109,677.76 $\text{cm}^{-1}$). Because he assumed a physical picture for the orbits, Bohr was able to make the calculations from other physical properties without using the Rydberg constant.

let end of the spectrum, *i.e.*, where there is more energy per quantum (light particle (Fig. 106)).

There is for hydrogen, therefore, a whole series of spectral lines made possible by jumps between any two of a number of energy levels.

Now Balmer (1885) and Rydberg had previously established an experimental rule for the positions of these lines in the hydrogen spectrum. Rydberg pointed out that there were thirty-two different lines whose wave lengths could be represented by the expression $(R_H/2^2) - (R_H/n^2)$, where $n = 3, 4, 5 \cdots 34$. According to Bohr's picture these would be just the energies expected from electrons jumping back to orbit 2 from orbits $3, 4, 5 \cdots 34$. Bohr thus gave a physical interpretation to the Rydberg expression. How good this agreement is, may be seen in Table 53.

TABLE 53. BALMER SERIES FOR HYDROGEN

| $n$ | Observed Wave Lengths | Calculated Wave Lengths |
|---|---|---|
| 3 | 6562.79 Å | 6562.80 Å |
| 4 | 4861.33 | 4861.38 |
| 5 | 4340.47 | 4340.51 |
| *etc.* | *etc.* | *etc.* |

(Wave lengths are expressed in Ångstrom units, where 1 Å is $10^{-8}$ cms.)

This principal quantum number, $n$, indicates the distance of the circular orbit from the nucleus. The distance is given by $n^2$; that is, the distance from the nucleus for orbits 1, 2, 3, and 4 would be 1, 4, 9 and 16 units respectively.

**261. Azimuthal Quantum Number, $l$.**—Improvement in spectroscopic analysis revealed that Bohr's circular orbits did not account for all spectral lines. It was necessary to assume that each circular orbit was subdivided into elliptical and circular orbits. These orbits are indicated by the letters **s, p, d, f,** the letters originally being chosen to represent the type of spectra obtained from them, *i.e.*, *sharp*, *principal*, *diffuse* and *fundamental* lines. The number which indicates this subdivision is called the **azimuthal quantum number, $l$,** and represents the eccentricity of the orbit.

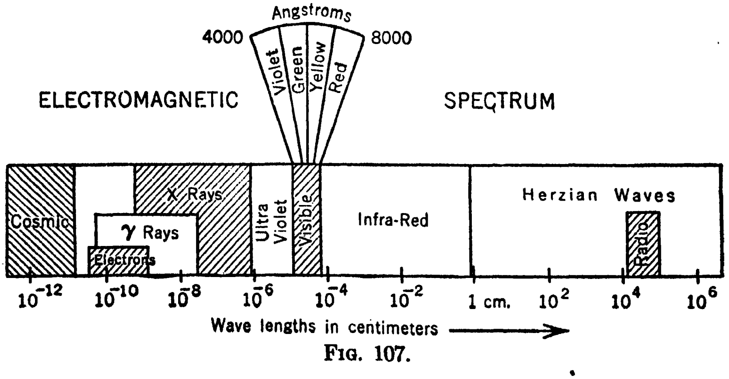

FIG. 107.

There are only as many values as the number of the orbit; for example orbit 3 can have 3 values, *i.e.*, 3s, 3p, and 3d. Orbit 2 has two values, *i.e.*, 2s and 2p.

Electrons can jump from one principal quantum number to a lower principal quantum number; but there is a choice of jumps. For instance, an electron jumping from orbit 4p might reach 4p → 3s, or 4p → 3d. Since both of these orbits, 3s and 3d, have about the same energy content, the two spectral lines would be very close together, and could not be distinguished from a single line except by a very delicate spectroscope. *Also, a great many possible jumps are "forbidden,"* that is, they are never observed to occur at all. For instance, a jump between orbits with the same letter, *viz.* 4p → 3p, does not occur.

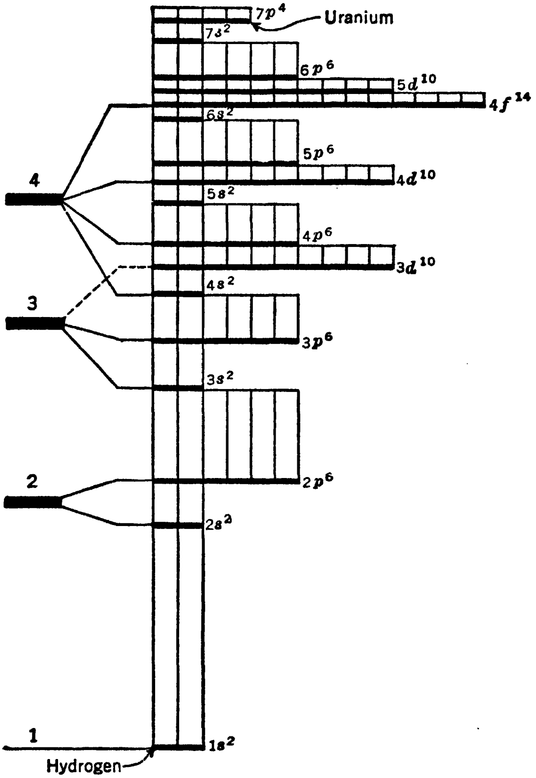

FIG. 108. Atomic orbitals. The lowest level is the most stable. Each box accommodates one electron. Each electron, added in succession in building up the 92 elements, goes into the lowest unoccupied box.

### DEMONSTRATION 88. SPECTRA

Materials: Salt cellars containing solid $BaCl_2$, $CuCl_2$, NaCl, and $SrCl_2$; red and green flares, burner, spectroscope aligned with the burner flame, spectral plates.

Each element has its own complex system of orbital electrons. Each element therefore gives off its own characteristic spectrum corresponding to changes in the positions of these orbits.

Some elements such as iron and manganese may have many thousands of spectral lines. The positions of these lines have been carefully measured, and interpreted in terms of transitions between the specific orbits described above.

**262. Two Magnetic Quantum Numbers, *m* and *s*.**—It was necessary to assume two other quantum numbers in order to explain all of the observed spectral lines. A **magnetic orbital number, *m*,** is a measure of a magnetic effect set up from the movement of an electron in its orbit (moving electricity creates a magnetic field). Also, it was necessary to assume (Uhlenback and Goudsmit, 1925) that the electron was spinning in its path, the magnetic field so produced being represented by a **spin quantum number, *s*.**

**263. The Pauli Exclusion Principle.**—The four quantum numbers described above are restricted in the values which they may assume, as shown in the following table.

TABLE 54. VALUES FOR THE FOUR QUANTUM NUMBERS

| Quantum Number | Symbol | Assumes Values | Physical Interpretation | Example |
|---|---|---|---|---|
| Principal | $n$ | $1, 2, 3 \cdots n$ | Distance of orbit from nucleus | $n = 3$ |
| Azimuthal | $l$ | s, p, d, $\cdots n$ where s = 0, p = 1, d = 2 | Ellipticity of orbit | If $n = 3$, $l$ can be s, p, d (*i.e.*, 0, 1, 2). |
| Magnetic orbital | $m$ | $0, \pm 1, \pm 2 \cdots \pm l$ | Magnetic field due to electron path | if $l = 2$, $m$ can have the values $0, +1, -1, +2, -2$ |
| Spin | $s$ | $\pm \frac{1}{2}$ | Magnetic field from spin of electron | s = either $+\frac{1}{2}$ or $-\frac{1}{2}$ |

Any orbit can therefore be characterized by these four quantum numbers. Let us examine, for example, the different orbits possible for a system having the principal and azimuthal quantum numbers represented by 2p. These would be

| $n$ | $l = 1$ | $m$ | $s$ |
|---|---|---|---|
| 2 | p | 0 | $+\frac{1}{2}$ |
| 2 | p | 0 | $-\frac{1}{2}$ |
| 2 | p | +1 | $+\frac{1}{2}$ |
| 2 | p | +1 | $-\frac{1}{2}$ |
| 2 | p | −1 | $+\frac{1}{2}$ |
| 2 | p | −1 | $-\frac{1}{2}$ |

There is thus a total of six different orbits. According to a rule formulated by Pauli, **no atom can have two electrons with the same set of quantum numbers.** This is known as the **Pauli Exclusion Principle.** Since only the foregoing six configurations are possible for 2p it follows that the maximum number of electrons in the 2p orbit is 6.

**264. Planetary Structure of the Atom.**—*Summary of Sections 258–263: for the benefit of students who have not been assigned these sections:*

**a.** Outside of the nucleus of the atom, electrons arrange themselves in definite orbits, numbered 1, 2, 3, 4, and so on up to $n$. This is called the **principal quantum number, $n$.**

**b.** These orbits may be round or elliptical. To designate different orbits having the same principal quantum number, the letters **s, p, d, f** and **g** are used. When $n = 2$ there are 2 orbits, *i.e.*, 2s and 2p; when $n = 4$ there are 4 orbits, *i.e.*, 4s, 4p, 4d, 4f; $n = 5$ would have 5 orbits and so on.

**c.** Only a limited number of electrons can be present for each letter. This number can be calculated, and turns out to be as indicated in the superscripts in the following plan.

$$\underbrace{1\mathrm{s}^2}_{2} \qquad \underbrace{2\mathrm{s}^2 \quad 2\mathrm{p}^6}_{8} \qquad \underbrace{3\mathrm{s}^2 \quad 3\mathrm{p}^6 \quad 3\mathrm{d}^{10}}_{18} \qquad \underbrace{4\mathrm{s}^2 \quad 4\mathrm{p}^6 \quad 4\mathrm{d}^{10} \quad 4\mathrm{f}^{14}}_{32}.$$

**d.** Planetary structure is built up by adhering to these rules: in each case the electron goes to whatever orbit of least energy is available. Thus hydrogen has the simplest structure, $1s^1$. Helium, with two electrons, has the structure $1s^2$. Lithium, with three electrons, has the structure $1s^2$, $2s^1$. Sodium, with 11 electrons, has the structure $1s^2$, $2s^2$, $2p^6$, $3s^1$. The electronic arrangement for all of the 92 elements is given in Table 55.

Some anomalies will be noticed in the table. For example when we come to potassium $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^1$, we find its outermost electron skips the 3d orbit and enters the 4s orbit. This is because the energy content of the 3d orbit is more than the 4s orbit, and this 19th electron of potassium seeks the orbit of minimum energy. The same is true for calcium. The next element, scandium, however, has its 21st electron in the 3d position. Scandium is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^1$, $4s^2$. See Fig. 108.

**265. Compound Formation by Electrovalence.**—The formation of compounds by give-and-take of electrons has already been taken up in detail (55). The formation of a stable molecule depends upon **the ability of the planetary electrons of the constituent atoms to form the nearest inert gas configuration.** Thus a sodium atom, $1s^2$, $2s^2$, $2p^6$, $3s^1$, written 2–8–1 for simplicity, combines with a chlorine atom (2–8–7) to form a sodium ion (2–8) and a chloride ion (2–8–8); these latter are identical with the

## TABLE 55. MODIFIED BOHR-THOMSEN ARRANGEMENT OF PLANETARY ELECTRONS FOR THE ELEMENTS

**SERIES ONE**

| | | 1 |
|---|---|---|
| | | *s* |
| 1 | H | 1 |
| 2 | He | 2 |

**SERIES TWO**

| | | 1 | 2 | |
|---|---|---|---|---|
| | | | *s* | *p* |
| | | 2 | | |
| 3 | Li | | 1 | |
| 4 | Be | | 2 | |
| 5 | B | | 2 | 1 |
| 6 | C | | 2 | 2 |
| 7 | N | | 2 | 3 |
| 8 | O | | 2 | 4 |
| 9 | F | | 2 | 5 |
| 10 | Ne | | 2 | 6 |

**SERIES THREE**

| | | 1 | 2 | 3 | |
|---|---|---|---|---|---|
| | | | | *s* | *p* |
| | | 2 | 8 | | |
| 11 | Na | | | 1 | |
| 12 | Mg | | | 2 | |
| 13 | Al | | | 2 | 1 |
| 14 | Si | | | 2 | 2 |
| 15 | P | | | 2 | 3 |
| 16 | S | | | 2 | 4 |
| 17 | Cl | | | 2 | 5 |
| 18 | A | | | 2 | 6 |

**SERIES FOUR**

| | | 1 | 2 | 3 | | | 4 | |
|---|---|---|---|---|---|---|---|---|
| | | | | *s* | *p* | *d* | *s* | *p* |
| | | 2 | 8 | 2 | 6 | | | |
| 19 | K | | | | | | 1 | |
| 20 | Ca | | | | | | 2 | |
| 21 | Sc | | | | | 1 | 2 | |
| 22 | Ti | | | | | 2 | 2 | |
| 23 | V | | | | | 3 | 2 | |
| 24 | Cr | | | | | 5 | 1 | |
| 25 | Mn | | | | | 5 | 2 | |
| 26 | Fe | | | | | 6 | 2 | |
| 27 | Co | | | | | 7 | 2 | |
| 28 | Ni | | | | | 8 | 2 | |
| 29 | Cu | | | | | 10 | 1 | |
| 30 | Zn | | | | | 10 | 2 | |
| 31 | Ga | | | | | 10 | 2 | 1 |
| 32 | Ge | | | | | 10 | 2 | 2 |
| 33 | As | | | | | 10 | 2 | 3 |
| 34 | Se | | | | | 10 | 2 | 4 |
| 35 | Br | | | | | 10 | 2 | 5 |
| 36 | Kr | | | | | 10 | 2 | 6 |

**SERIES FIVE**

| | | 1 | 2 | 3 | 4 | | | 5 | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | *s* | *p* | *d* | *s* | *p* |
| | | 2 | 8 | 18 | 2 | 6 | | | |
| 37 | Rb | | | | | | | 1 | |
| 38 | Sr | | | | | | | 2 | |
| 39 | Y | | | | | | 1 | 2 | |
| 40 | Zr | | | | | | 2 | 2 | |
| 41 | Cb | | | | | | 4 | 1 | |
| 42 | Mo | | | | | | 5 | 1 | |
| 43 | Ma | | | | | | 6 | 1 | |
| 44 | Ru | | | | | | 7 | 1 | |
| 45 | Rh | | | | | | 8 | 1 | |
| 46 | Pd | | | | | | 10 | | |
| 47 | Ag | | | | | | 10 | 1 | |
| 48 | Cd | | | | | | 10 | 2 | |
| 49 | In | | | | | | 10 | 2 | 1 |
| 50 | Sn | | | | | | 10 | 2 | 2 |
| 51 | Sb | | | | | | 10 | 2 | 3 |
| 52 | Te | | | | | | 10 | 2 | 4 |
| 53 | I | | | | | | 10 | 2 | 5 |
| 54 | Xe | | | | | | 10 | 2 | 6 |

**SERIES SIX**

| | | 1 | 2 | 3 | 4 | | | | 5 | | | 6 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | *s* | *p* | *d* | *f* | *s* | *p* | *d* | *s* | *p* |
| | | 2 | 8 | 18 | 2 | 6 | 10 | | | | | | |
| 55 | Cs | | | | | | | | 2 | 6 | | 1 | |
| 56 | Ba | | | | | | | | 2 | 6 | | 2 | |
| 57 | La | | | | | | | | 2 | 6 | 1 | 2 | |
| 58 | Ce | | | | | | | 1 | 2 | 6 | 1 | 2 | |
| 59 | Pr | | | | | | | 2 | 2 | 6 | 1 | 2 | |
| 60 | Nd | | | | | | | 3 | 2 | 6 | 1 | 2 | |
| 61 | Il | | | | | | | 4 | 2 | 6 | 1 | 2 | |
| 62 | Sm | | | | | | | 5 | 2 | 6 | 1 | 2 | |
| 63 | Eu | | | | | | | 6 | 2 | 6 | 1 | 2 | |
| 64 | Gd | | | | | | | 7 | 2 | 6 | 1 | 2 | |
| 65 | Tb | | | | | | | 8 | 2 | 6 | 1 | 2 | |
| 66 | Ds | | | | | | | 9 | 2 | 6 | 1 | 2 | |
| 67 | Ho | | | | | | | 10 | 2 | 6 | 1 | 2 | |
| 68 | Er | | | | | | | 11 | 2 | 6 | 1 | 2 | |
| 69 | Tm | | | | | | | 12 | 2 | 6 | 1 | 2 | |
| 70 | Yb | | | | | | | 13 | 2 | 6 | 1 | 2 | |
| 71 | Lu | | | | | | | 14 | 2 | 6 | 1 | 2 | |
| 72 | Hf | | | | | | | 14 | 2 | 6 | 2 | 2 | |
| 73 | Ta | | | | | | | 14 | 2 | 6 | 3 | 2 | |
| 74 | W | | | | | | | 14 | 2 | 6 | 4 | 2 | |
| 75 | Re | | | | | | | 14 | 2 | 6 | 5 | 2 | |
| 76 | Os | | | | | | | 14 | 2 | 6 | 6 | 2 | |
| 77 | Ir | | | | | | | 14 | 2 | 6 | 7 | 2 | |
| 78 | Pt | | | | | | | 14 | 2 | 6 | 9 | 1 | |
| 79 | Au | | | | | | | 14 | 2 | 6 | 10 | 1 | |
| 80 | Hg | | | | | | | 14 | 2 | 6 | 10 | 2 | |
| 81 | Tl | | | | | | | 14 | 2 | 6 | 10 | 2 | 1 |
| 82 | Pb | | | | | | | 14 | 2 | 6 | 10 | 2 | 2 |
| 83 | Bi | | | | | | | 14 | 2 | 6 | 10 | 2 | 3 |
| 84 | Po | | | | | | | 14 | 2 | 6 | 10 | 2 | 4 |
| 85 | | | | | | | | 14 | 2 | 6 | 10 | 2 | 5 |
| 86 | Rn | | | | | | | 14 | 2 | 6 | 10 | 2 | 6 |

**SERIES SEVEN**

| | | 1 | 2 | 3 | 4 | 5 | 6 | | | 7 |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | *s* | *p* | *d* | |
| | | 2 | 8 | 18 | 32 | 18 | 2 | 6 | | |
| 87 | | | | | | | | | | 1 |
| 88 | Ra | | | | | | | | | 2 |
| 89 | Ac | | | | | | | | 1 | 2 |
| 90 | Th | | | | | | | | 2 | 2 |
| 91 | Pa | | | | | | | | 3 | 2 |
| 92 | U | | | | | | | | 4 | 2 |

electronic configuration for neon (2–8) and argon (2–8–8), the nearest inert gases (Figs. 25, 26, pages 83, 85).

Since the Na atom loses an electron, it becomes positively charged, *i.e.*, $Na^+$; and since the Cl atom gains an electron, it becomes negatively charged, *i.e.*, $Cl^-$. This type of valence bond between the elements in a compound is called **electrovalence**, for the two particles are obviously electrically charged, and will conduct electricity.

**266. Compound Formation by Covalence.**—Two atoms of chlorine can form the stable molecule $Cl_2$. How is this possible? For Cl (2–8–7) cannot possibly form an inert gas configuration by giving or taking up electrons from a second chlorine atom.

In this case, we are dealing with another type of bond, **covalence.** This involves a **sharing of electron pairs.** Here the two chlorine atoms share a pair of their outermost electrons, assuming a quasi-inert gas configuration. This is shown for a number of compounds in Fig. 109 where only the outermost shell is indicated. Most carbon compounds such as $CH_4$, $CCl_4$, $CH_3Cl$, $CS_2$, $C_3H_8$ are linked by covalent bonds. **It will be noticed that the electrons are shared in pairs, and that there is a shell of 2 or 8 electrons around each atom.**[1]

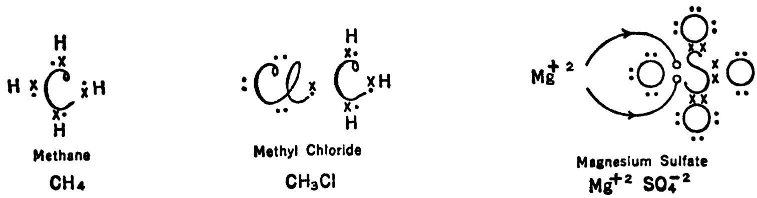

FIG. 109. Covalent bonds in methane and methyl chloride. Electrovalent and covalent bonds in magnesium sulfate.

For a number of compounds the student will be unable to decide the type of binding without more information. Thus $CH_4$ could be, but is not, linked by electrovalent bonds. An important criterion of the presence of electrovalent bonds is the ability of the compound to conduct an electric current.

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[1] Molecular oxygen is abnormal. It is not joined by two simple electron pairs. To account for its peculiar magnetic properties Pauling (1931) proposed a structure with one electron-pair bond and two three-electron bonds, *i.e.*, $\left[ :\overset{\cdot\;\cdot\;\cdot}{\underset{\cdot\;\cdot\;\cdot}{O:O}}: \right]$

### DEMONSTRATION 89. CONDUCTIVITY AND TYPE OF BONDS

Materials: Three aqueous solutions of salts, such as $NaCl$, $MgCl_2$, $Ca(NO_3)_2$; three non-electrolytes or solutions of salts in non-electrolytes, each solution containing two electrodes connected in series with a Christmas tree bulb; the six pairs of electrodes connected in parallel to 110 volts D.C. or A.C.

It is observed that the presence of electrovalent bonds makes it possible to conduct current, three of the bulbs lighting up, the remaining three bulbs indicating that no current is flowing.

**All salts, by definition, contain electrovalent bonds, and therefore conduct.** $MgSO_4$, for example, contains both electrovalent and covalent bonds. The $Mg^{++}$ is bound to the $SO_4^{=}$ by electrovalence: when a current is passed the $Mg^{++}$ migrates to the negative pole, while the $(SO_4)^{=}$ appears at the positive pole. On the other hand, the $S^{+6}$ and $O^{-2}$ are linked by covalence, for they move as a unit towards the positive pole, instead of the $S^{+6}$ going in one direction and the $O^{-2}$ moving in the other. This, too, is illustrated in the figure.

## QUESTION REVIEW

### PHENOMENA CONNECTED WITH THE PLANETARY ELECTRONS

I. THE FOUR QUANTUM NUMBERS.

**a. Principal quantum number, *n* (260).**

1. How did Bohr depend upon Einstein and Rutherford? What does the principal quantum number indicate?
2. Show how Bohr's postulates give a physical interpretation to the Rydberg expression.

**b. Azimuthal quantum number, *l* (261).**

3. How many letters are possible with a principal quantum number of 5?
4. In what way did an increase in the sensitivity of spectroscopes reveal that one quantum number was insufficient?

**c. Two magnetic quantum numbers, *m* and *s* (262).**

5. Give a physical interpretation to the two quantum numbers *m* and *s*.

**d. The Pauli exclusion principle (263).**

6. State the Pauli exclusion principle. Show that it predicts that there can be only two electrons in the first orbit.
✓ 7. Write the ten sets of quantum numbers belonging to the *d*-orbit.

**e. Planetary structure of the atom (264).**

8. Give the planetary electron structure of the three isotopes of oxygen, $^{16}_{8}O$, $^{17}_{8}O$ and $^{18}_{8}O$. Also indicate their nuclear structure.
9. Account for the fact that calcium has two electrons in orbit 4, but none in orbit 3*d*.

II. THE FORMATION OF COMPOUNDS.

**a. Electrovalence (265).**

10. Draw the electronic configurations for $MgCl_2$, for $AlF_3$, and for MgO.

**b. Covalence (266).**

11. Draw the outer shells for each atom in the following compounds. They are linked by covalence. $CH_4$, $CHCl_3$, $CO_2$, $H_2$, $F_2$.

12. Show the electron arrangement in the compound NaOH. What experimental evidence can you advance to show that the O and H are linked by covalence, whereas the Na is linked by electrovalence to the OH?
13. Write the electronic arrangement in $Na_2CO_3$. In $MgSO_4$.

**Reading Reference:** Article number 406 in the Appendix.

# PART III: INORGANIC CHEMISTRY

The Inert Gases
The Periodic Table
The Metals
The Non-Metals

# CHAPTER XXI

# THE ATMOSPHERE

**267. The Atmosphere has Weight.**—The word **atmosphere** (Greek, *vapor* + a *sphere*) refers to the great ocean of aeriform fluid surrounding the earth, and commonly called the air. The latter term was used by the older chemists in the same sense as we now employ the word "gas."

DEMONSTRATION 90. ATMOSPHERIC PRESSURE

Materials: Gallon tin-can containing pint of water, set on tripod over burner; rubber stopper for can; gloves, pail of water.

That the air has weight (approximately 15 pounds per square inch) may be demonstrated by boiling the water in the can, stoppering tightly, and immersing it in cold water. The steam condenses, and the weight of the 100 miles of air above the can collapses it (Fig. 110). A cubic foot of air weighs just a little more than the letter the postman carried for three cents.

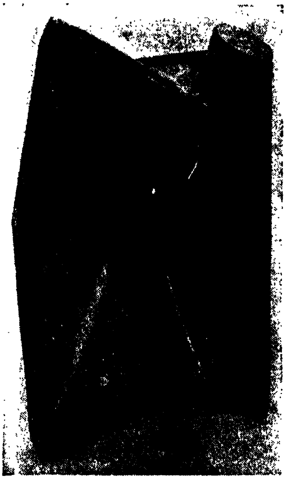


FIG. 110. Can crushed by atmospheric pressure (Dem. 90).

**268. Air is a Mixture.**—Air is a mixture, not a compound, because

(*a*) The composition of the air varies more or less from time to time, consequently its composition cannot be represented by means of a chemical formula. Every chemical compound, on the other hand, is definite in composition (see Law of Definite Proportions).

(*b*) The components of the air retain their own properties.

(*c*) The components of the air may be separated by mechanical means. Thus, when liquid air is allowed to evaporate, the more volatile nitrogen escapes first, leaving a residue richer and richer in oxygen.

An analysis of the substances in the air is given in Table 56.

In addition to this there are traces of nitrogen compounds such as ammonia, oxides of nitrogen and nitric acid; traces of ozone or hydrogen peroxide; and small quantities of industrial gases such as sulfur dioxide and hydrogen sulfide. Dust and bacteria vary according to locality. Also there are up to 20,000 free ions in each cubic foot of air.

TABLE 56. APPROXIMATE PERCENTAGE COMPOSITION OF THE AIR

(by volume)

| | | | |
|---|---|---|---|
| Nitrogen | 78 | Inert gases as follows: | |
| Oxygen | 21 | Argon | 0.94 |
| Carbon dioxide | 0.03 | Neon | 0.001 8 |
| Hydrogen | 0.000 1 | Helium | 0.000 5 |
| | | Krypton | 0.000 1 |
| | | Xenon | 0.000 009 |

Water vapor is not included in the above percentages. It is about 2%, and varies from day to day.

**269. Bacteriology of the Air.**—Some of the dust in the air is organic, a part of which consists of microscopic organisms (spores of molds and yeasts, bacteria, etc.). There are from 4 to 5 microbes, on an average, in one liter of air, whereas pure unfiltered river water contains from 6,000 to 20,000 in one cc., and natural soil about 100,000 per cc. It should be noted that bacteria do not find their way into the air from a moist surface. When the soil is dry and wind currents are strong, bacteria pass into the atmosphere. After a prolonged rain, the air contains but few bacteria. The spores of molds are very abundant, however, during warm, damp weather. The most dangerous factor, hygienically, is probably dust to which bacteria cling. This is particularly true of dust of dwellings, which may carry infectious microbes, such as the *tubercle bacillus.* Most of the microbes of the air, however, are saprophytic, such as the organisms producing fermentation and putrefaction. Dust can be removed from air by drawing it through wide tubes packed with 12–15 inches of cotton.

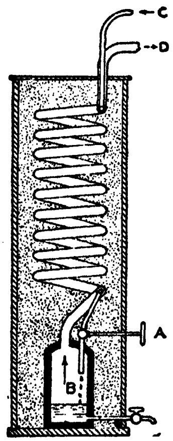


FIG. 111. Liquefaction of air.

**270. Liquid Air.**—Liquid air is now produced on a large scale by a method invented independently by Hampson and by Linde. This method is based upon the fact that, **when a gas under high pressure is allowed to expand through a small orifice, some of the heat energy of the gas is used up in overcoming the cohesion of the molecules and in separating them farther apart.** The following is a brief outline of the process:

The air is first freed of carbon dioxide by means of lime, after which it is compressed to 200 atmospheres. The heat generated by the compression of the gas is now absorbed by allowing the compressed gas to flow through pipes cooled by running water. As a consequence of the compression, most of the water vapor of the air is condensed; but the last traces of water vapor and carbon dioxide are removed by the use of solid sodium hydroxide. The air is now allowed to pass to the liquefier, the essential part of which is two concentric metal pipes wound in the form of a spiral, and well protected by means of a non-conductor of heat (Fig. 111). The highly compressed air is pumped down the inner tube (*C*) and allowed to escape through a small orifice in the bottom. The gas therefore expands and its temperature falls. The cold gas now passes up the outer tube (*BD*), and is again compressed and pumped back through the inner tube. While the gas is passing upward it cools the compressed air passing down the inner tube. The cold compressed gas is again allowed to expand, and consequently becomes still colder. This process is repeated until the gas liquefies. The liquid air is withdrawn from time to time by means of a valve.

Some of the modern methods for liquefying air achieve the process in a single expansion step.

Liquid air is stored in **Dewar flasks,** commonly known as thermos bottles. These flasks consist of one glass flask surrounded by another, the space between their walls being evacuated. The inner wall of the outer flask may be silvered in order to reflect the radiant energy of surrounding bodies.

The largest single use for liquid air is the production of oxygen. Liquid air is used to shrink the inserts in the exhaust-valves of the Ford V-8 so that they can be pushed through the holes in the valves.

### DEMONSTRATION 91. LIQUID AIR IS COLD

Materials: (*a*) Coffee-pot on cake of ice; (*b*) two 6 mm. tubes, one drawn to a nozzle, passing through a stopper to the bottom of a pyrex test-tube, rubber policeman, rubber tubing leading to illuminating gas; (*c*) cotton string tied to 50 g. weight lowered into a test-tube of such size as to fit a candlestick; scissors, kerosene.

The coldness of liquid air is illustrated in the following experiments. (a) Liquid air in a coffee pot on ice "boils," and "dry ice" is frozen out as a ring on the bottom of the pot, from the carbon dioxide in the atmosphere. (b) The methane in illuminating gas blown through the empty test-tube, immersed in liquid air, solidifies. Disconnect the rubber tubing and replace it with the rubber policeman. The solid methane will now evaporate and may be lighted at the nozzle. Warming the tube in the hand increases the flame. (c) Kerosene in a test-tube (*Danger: do not allow kerosene to come into contact with liquid air; such a mixture would be violently explosive*) into which the weight and cord have been lowered, will freeze solidly when the tube is lowered into liquid air. Hold under a water tap for a moment, pull out the solid "kerosene candle," set it in its stand, trim the wick, and light. Note: the mercury hammer experiment works better with carbon dioxide (Demonstration 128, Section 494).

DEMONSTRATION 92. PROPERTIES CHANGE AT LOW TEMPERATURE

Materials: Cranberries, carnations, hot-dog, rubber ball, coil of solder attached to a small weight, two test-tubes of solid potassium dichromate, beefsteak, hammer, three 400 cc. beakers.

Substances such as beefsteak, eggs and flowers become brittle when immersed in liquid air. A rubber ball shatters like glass. Cranberries rattle in the beaker and feel icy-cold. Some colored solids turn pale. Lead solder becomes springy.

DEMONSTRATION 93. OXYGEN RESIDUE FROM BOILING AIR

Materials: Four 100 cc. beakers, cotton, cigar, tongs, cigarettes, splint, charcoal, steel spring. See Demonstration 12, page 49.

When liquid air boils, most of the nitrogen escapes. Combustible materials immersed in the residual liquid oxygen burn vigorously (*Care: Protect face*). Cigars are consumed so rapidly that no odor is given off; cigarettes leave little ash, and show the deep lithium and potassium flames. *Caution: do not ignite a mixture of aluminum and liquid air; this is dangerously explosive.*

DEMONSTRATION 94. LIQUID AIR IS OFTEN HARMLESS

Materials: Cylinder of water, goldfish, net, sieve.

Liquid air may be poured over the hands without fear, since it forms an insulating layer of gas, called the Crooke's layer, similar to that formed by a drop of water on a hot stove. Also, it may be squirted into the mouth (*Caution: do not allow a solid object containing the air to touch the mouth*). Finally, a goldfish may be dropped into the liquid air for 15 seconds (no longer). While it appears frozen to death, it quickly revives when returned to its cylinder of water. Such fish often lose their tails and fins after this experiment; but within a fortnight new appendages have grown in and the goldfish seem none the worse for their experience.

**271. The Oxygen-Carbon Dioxide Cycle.**—Carbon dioxide is found in all specimens of air, the main sources of the gas being the combustion of fuel, the decay of vegetable and animal matter, and the process of breathing. Pure country air contains about 3 vols. of carbon dioxide per 10,000 vols. of air; and in large cities where much coal is burned, the amount of the gas may rise to 6–7 vols. per 10,000 vols. Rooms crowded with people sometimes contain as high as 50 vols. of carbon dioxide per 10,000 vols. of air.

Although huge quantities of coal are burned each year, the percentage of carbon dioxide in the atmosphere is relatively constant because of the so-called **oxygen-carbon dioxide cycle.** In the first phase of the cycle, the oxidation of carbon compounds in the bodies of animals produces carbon dioxide, water and a considerable quantity of energy. Enough energy is liberated by burning a pound of fat to lift a 150 pound man to a height of 16 miles into the air. The cycle involving sugar (glucose) is:

$$\begin{tikzcd}
 & \text{plants} \arrow[dr] & \\
6H_2O + 6CO_2 \arrow[ur] & & C_6H_{12}O_6 \text{ (glucose)} + 6O_2. \arrow[dl] \\
 & \text{animals} \arrow[ul] &
\end{tikzcd}$$

Animal respiration releases this carbon dioxide and water vapor into the air. Man, for example, inhales an average of 21% $O_2$, 0.03% $CO_2$; and exhales 16% $O_2$, 4% $CO_2$. In the second phase of the cycle, plants reverse the process. Chlorophyll, the green coloring matter of the plant, absorbs energy in the form of sunlight and converts $H_2O$ and $CO_2$ into sugar. This plant process is called photosynthesis. The cycle of animal respiration and plant photosynthesis continues indefinitely, and thus maintains a constant percentage of oxygen and carbon dioxide in the air.

### DEMONSTRATION 95. OXYGEN-CARBON DIOXIDE CYCLE

Materials: Green plants crushed into a test-tube filled with water and inverted in a crystallizing dish; calcium hydroxide, test-tubes, soda straws, splint, clock-glass.

Green leaves will continue to give off oxygen as the result of the above photosynthesis; and this oxygen may be tested with a glowing splint. On the other hand, the presence of carbon dioxide in the air is shown when a clock-glass containing limewater (calcium hydroxide) is exposed to the atmosphere; in a few minutes a white coating of calcium carbonate is formed:

$$\underset{\text{limewater}}{Ca(OH)_2} + \underset{\text{in air}}{CO_2} \rightarrow \underset{\text{milky chalk}}{CaCO_3} \downarrow + H_2O.$$

Similarly, breathing into limewater will demonstrate the presence of carbon dioxide in the breath.

**272. The Nitrogen Cycle.**—Nitrogen is essential for the growth of plants and animals. It is present in the form of the amine group, $-NH_2$, in all proteins; and the waste products of animals contain combined nitrogen: *e.g.*, urea, $(NH_2)_2CO$. Animals cannot assimilate free nitrogen, but they obtain it from nitrogenous foods—vegetable or animal. Most plants secure the required nitrogen from fertilizers—ammonium nitrate, manure, etc.—supplied to the soil. Certain plants, however, particularly the leguminosae (peas, beans, clover, etc.), are able to assimilate free nitrogen. Symbiotic bacteria appear to live as guests in the nodules on the roots of these plants, and they are able to convert free atmospheric nitrogen into complex substances needed for the growth of the plants. This fact is of very great importance in agriculture. Thus, when clover is plowed under, the soil is enriched.

Nitrogen undergoes a never-ceasing cycle of changes in nature (Fig. 112). Starting with free atmospheric nitrogen, it may be fixed by electrical discharge or by symbiotic bacteria, and thus rendered available as plant food. Plants serve as food for animals; and when plants and animals die and decay, ammonia, nitrates, nitrogen, etc., are formed. The nitrogen compounds enrich the soil for living plants, and the free nitrogen, returned to the air, repeats the cycle over and over through countless ages.

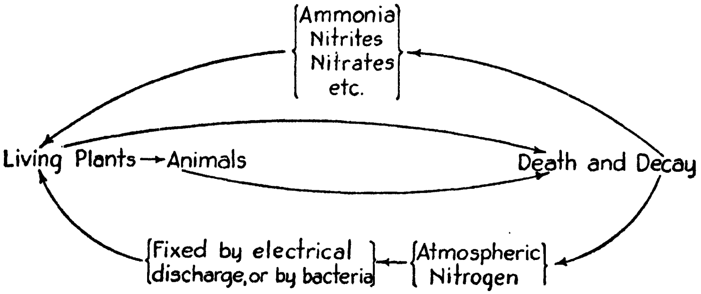


FIG. 112. The nitrogen cycle.

"There is no atom of nitrogen in the air that has not at some time or other in the course of its existence throbbed through the tissues of a living plant or animal, not once but many times."

**273. Water Vapor.**—The amount of water present in the average room on a hot summer day is about three pounds, or a quart and a half. **When air is saturated with water vapor, the humidity is 100 per cent.** The average humidity is about 66 per cent. Why is there so much discomfort on a hot, humid day? This is due to the combination of high temperature and excessive humidity, which retards evaporation of perspiration from the skin. Ventilation or fanning affords relief, for evaporation is hastened;

and this not only uses up heat, but removes the stationary layer of air next to the skin.

When the temperature of saturated air is lowered, the water vapor condenses in droplets as dew, fog, or clouds; or it may be precipitated in the form of rain, snow, or hail. More than 140,000 tons of rain would be deposited by cooling one cubic mile of saturated air from 35° to 0°.

Air may be dried by drawing it through tubes containing a dehydrating agent, such as calcium chloride or phosphorus pentoxide; or through a trap consisting of a bulb immersed in liquid air to freeze out the water.

## THE HELIUM GROUP

**274. Relationships of the Helium Family.**—This group of elements is listed in Table 57. The members are monatomic, colorless gases; and since their sub-orbits are completed, they have a valence of zero; that is, they are chemically inert. They were discovered and identified by means of their characteristic spectra.

Recently a number of unusual compounds of the helium family have been reported: HeH, HgHe, $WoHe_2$, $A(BF_3)$, $A(BF_3)_2$, $A(BF_3)_6$, and Kr, $5H_2O$.

TABLE 57. THE HELIUM FAMILY

| Element | At. Wt. | At. No. | Electronic Structure | B.P. | M.P. | C.T. |
|---|---|---|---|---|---|---|
| Helium, He | 4.00 | 2 | 2 | −268.9° | −272.2° | −267.9° |
| Neon, Ne | 20.18 | 10 | 2-8 | −246° | −248.67° | −228.7° |
| Argon, A | 39.94 | 18 | 2-8-8 | −185.7° | −189.2° | −122.4° |
| Krypton, Kr | 83.7 | 36 | 2-8-18-8 | −153° | −157° | − 62.6° |
| Xenon, Xe | 131.3 | 54 | 2-8-18-18-8 | −107.2° | −112° | + 16.6° |
| Radon, Rn | 222.0 | 86 | 2-8-18-32-18-8 | − 61.8° | − 71° | +104.4° |

**275. Argon, A.**—Argon (Greek, *idle, inactive*) is the most abundant member and the first member of the family to be discovered on earth. Lord Rayleigh showed that a liter of nitrogen obtained from the air weighed 1.2572 g., whereas a liter of the gas prepared from different nitrogen compounds—ammonia, urea, etc.—had a mean weight of only 1.2505 g. Although this difference does not exceed one-half of one per cent, it still is much greater than the experimental error.

Now Cavendish had noticed a full hundred years previous to this (1785) that if air sparked with oxygen in the presence of "soap lees" (alkali, to absorb the nitric acid formed), 1/120th of the original volume failed to be affected. Rayleigh adopted the hypothesis that this 1/120th was probably some unknown gas, heavier than nitrogen, which increased the weight of atmospheric nitrogen to 1.2572. He repeated and confirmed Cavendish's experiments. To obtain this unknown gas Rayleigh and Ramsay passed atmospheric nitrogen over magnesium to form magnesium nitride ($Mg_3N_2$); a small portion of the gas did not combine with the magnesium. The spectrum of this residual gas was unlike that of any known element, so in 1894 **argon** was announced to the world.

Today this inert gas has found a use in industry. All tungsten-filament bulbs over 15-watt capacity are filled with argon to retard the evaporation of tungsten from the hot filament, and to thus prolong the life of the bulb.

**276. Helium, He.**—The element helium (Greek, *the sun*) was discovered in the sun through spectroscopic observation of its prominent orange line by the French astronomer Janssen during the solar eclipse on August 18, 1868, and from the subsequent suggestions of the English scientists Lockyer and Frankland.

In 1895 Ramsay learned that Hillebrand, chemist of the United States Geological Survey, had obtained a gas from the mineral *uraninite*, which to the latter appeared to be nitrogen. Ramsay secured a specimen of uraninite (clevite), heated it with sulfuric acid, collected the gas, and determined its spectrum, which was found to be identical with that of solar helium.

Helium constitutes 1.75 of the natural gas at Amarillo, Texas, where there is enough to supply helium at its present rate of consumption for 180 years. After cooling to − 200° C., which freezes out all but the helium, the gas is compressed into cylinders at 160 atmospheres pressure. Cost of 15¢ a cubic foot in 1937 was reduced under governmental control to 1.425¢ by 1939.

In the New York City parks, hydrogen balloons are prohibited because of fire-hazard; so vendors fill balloons from a helium tank for 5¢ apiece; the same balloon thirty years ago would have cost $5,000. After the giant Zeppelin, the Hindenberg, exploded at Lakewood, N. J. (Fig. 21) in 1936, the United States Government refused shipment of helium for military purposes to Germany. In 1939 the government purchased the Dexter (Kansas) and Thatcher (Colorado) helium sources, and thereby gained a monopoly over our helium supply. Production at Amarillo in 1939 was 6,281,800 cubic feet, 90,541,000 cubic feet since the ten years of operation. Use is chiefly for meteorological and observation balloons, 1000 cubic feet of helium lifting 65 pounds, compared with 76 pounds for hydrogen. Largest non-government consumer was Goodyear Tire and Rubber Company, for pleasure balloons.

Hospitals in 1940 purchased one-quarter of all non-governmental helium, for use with anaesthetics, and treating asthma and other respiratory diseases. For more than a decade helium has been substituted for nitrogen in making a synthetic air for deep-sea divers; this use depends upon the insolubility of helium in the blood. Formerly the release of dissolved nitrogen from the blood caused severe, often fatal, pains known as "diver's bends" when the diver was brought quickly to the surface. Helium is also used for cooling high-speed generators; and as an atmosphere for annealing metals, because of its low solubility in metals.

Helium is the most difficult member of its family to liquefy. Below 2.2° A. its properties change abruptly: its thermal conductivity increases, its viscosity decreases, and it behaves like a gas.

**277. Neon Ne, Krypton Kr, Xenon Xe.**—Ramsay and Travers (1898) isolated the elements **neon** (Greek, *new*), **krypton** (Greek, *hidden*), and **xenon** (Greek, *stranger*) from crude argon prepared from the atmosphere. This was accomplished by liquefying the argon by means of liquid air, and then subjecting the clear liquid to fractional evaporation. The fractions containing these three inert gases were analyzed spectroscopically.

At present the inert gases, with the exception of helium, are prepared from the fractional distillation of liquid air. Krypton and helium can be absorbed in charcoal at − 190° C.; while platinum will occlude helium but not nitrogen or neon.

The so-called *neon sign* is an electric discharge through a tube containing various gases at a few mm. pressure. Neon alone gives a red glow in clear or opal glass. Deep blue is achieved with a mixture of argon and mercury; green, from argon in an amber tube; gold, from helium in a yellow tube; and brilliant white, from argon, neon and mercury. The *neon lamp* can attain either full brilliancy or complete extinction in a millionth of a second. By synchronizing its flashes with objects rapidly whirling with fast periodic motion, such as the parts of an automobile, the parts appear to stand still and may be examined while in rapid motion. Such a device is called a *stroboscope*.

The prices per cubic foot of these gases in 1939 were: argon, $2 commercial, $283 pure; krypton, $14,156; neon, $283; helium, 1.425 cents commercial, $283 pure; xenon, $18,000.

**278. Radon.**—Radium emanation or Radon, Rn, belongs to the family of rare gases. Ramsay and Gray, with only a tiny bubble of the gas at their disposal found its molecular weight to be 222. The production of helium and radon as radioactive disintegration products has already been discussed (249).

## QUESTION REVIEW

I. THE ATMOSPHERE.

**a. The atmosphere has weight** (267).

1. Estimate the total pressure of the atmosphere, in pounds, against the human body.

**b. Air is a mixture** (268).

2. Give three proofs that air is not a compound.
3. In the air, is there more carbon dioxide or more of the combined members of the helium family?

**c. Bacteriology of the air** (269).

4. Estimate the number of bacteria in a single breath. What other accidental components of the air are there?

II. LIQUID AIR (270).

5. Sketch the industrial liquefaction of air.
6. Outline three experiments to demonstrate each of four properties of liquid air.

III. ACTIVE SUBSTANCES IN THE AIR.

**a. The oxygen-carbon dioxide cycle** (271).

7. Write the equation for the burning of glucose, explaining its reversibility in the oxygen-carbon dioxide cycle.
8. Is it correct to say "man inhales oxygen, and breathes out carbon dioxide?"
9. What chemical reaction proves the presence of carbon dioxide in the air?

**b. The nitrogen cycle** (272).

10. Diagram the nitrogen cycle. Why does a farmer "rotate" crops?

**c. Water vapor** (273).

11. "It isn't the heat; it's the humidity." Why?
12. How is air dried?

IV. THE HELIUM FAMILY.

**a. Relationships of the helium family** (274).

13. Which two members of the family have the lowest boiling points? Can any be liquefied near room temperature at high pressures? Is there any parallelism between atomic weight and boiling point?

14. Helium has been solidified. How close to absolute temperature, then, has the scientist approached?
15. Is this statement correct: "The electronic shells are completely filled, so that none of the members of the helium family forms any compounds."

b. **Argon** (275).

16. Explain the sequence of events which led to Ramsay's discovery of argon. What is argon used for commercially?

c. **Helium** (276).

17. Account for the name of this element.
18. Give some helium statistics.
19. What is peculiar about helium at low temperatures?

d. **Neon, Krypton, Xenon** (277).

20. How are the inert gases separated from one another? How identified?
21. Describe some properties of discharge tubes containing members of the helium family.

e. **Radon** (278).

22. By the disintegration of what substance is radon formed? To what use has it been put (253)?

**Reading References:** Articles number 29, 102, 119, 203, 217, 242, 247, 317 and 401 in the Appendix.

# CHAPTER XXII

## CLASSIFICATION OF THE ELEMENTS

The classification of the elements has engaged the attention of chemists for more than a hundred years. A brief outline of some of the attempts at classification will be presented.

### CLASSIFICATION ACCORDING TO CHEMICAL PROPERTIES

**279. Metals and Non-Metals.**—The elements have long been classed as metals, or base-forming elements, and as non-metals, or acid-forming elements. This classification is far from ideal, for certain elements do not fall sharply into either class, *i.e.*, they possess both metallic and non-metallic characteristics, or are both basic and acidic in character: *e.g.*, arsenic and antimony. Such elements are sometimes called **metalloids, or amphoteric elements.**

Metals and non-metals do have certain general characteristics, however. Metals, *e.g.*, silver and gold, show what is known as a metallic luster; they are malleable, ductile, and are good conductors of electricity.

In general, the non-metals do not possess these characteristics. Metals, as a rule, have greater densities and higher melting points and boiling points than do the non-metals. There are conspicuous exceptions, however.

### CLASSIFICATION ACCORDING TO ATOMIC WEIGHTS

**280. Prout's Hypothesis.**—In 1815–1816 Prout, an English physician, proposed that all of the elements were built up of hydrogen. Since hydrogen has a weight of 1, this meant that the atomic weights of all of the elements should be whole numbers. The hypothesis soon appeared untenable, when the careful determinations of atomic weights by Berzelius, Dumas, Stas and others showed that some of the atomic weights were far from whole numbers: *e.g.*, that of chlorine is 35.5.

**281. Döbereiner's Triads.**—Between the years 1816 and 1829, J. W. Döbereiner noticed that certain chemically related elements possessed atomic weights which exhibited a constant difference when arranged in sets of three, *i.e.*, the atomic weight of the middle element is approximately the mean of the other two. The following sets of elements illustrate Döbereiner's triads:

| | *At. wts.* | | | *At. wts.* | |
|---|---|---|---|---|---|
| Chlorine | 35.46 | | Calcium | 40.08 | |
| Bromine | 79.92 | (81.19) | Strontium | 87.63 | (88.72) |
| Iodine | 126.92 | | Barium | 137.36 | |

The numbers in parentheses are the mean values of the two extremes.

Furthermore, Döbereiner showed that certain closely related elements have atomic weights which are very nearly the same: *e.g.*, the triad Fe (55.85), Co (58.94), and Ni (58.69).

**282. Newlands' Law of Octaves.**—J. A. R. Newlands (1863–1864) arranged the elements according to atomic weights, and observed that the chemical properties of every eighth element were alike; that is, "**members of the same group of elements stand to each other in the same relation as the extremities of one or more octaves in music.**" Newlands termed this striking relationship the **Law of Octaves.**

The following periods of elements will serve as illustrations:

| Li | Be | B | C | N | O | F |
|---|---|---|---|---|---|---|
| 7 | 9 | 11 | 12 | 14 | 16 | 19 |
| Na | Mg | Al | Si | P | S | Cl |
| 23 | 24 | 27 | 28 | 31 | 32 | 35.5 |

According to this arrangement of the elements, sodium is the seventh element after lithium, and these metals have similar properties. In the same way magnesium is the seventh after beryllium, aluminum after boron, silicon after carbon, etc. These pairs of elements therefore have similar properties.

However, in Newlands' day scarcely two-thirds of the 92 elements were known; and since he did not leave blanks for undiscovered elements, his octaves in some cases were rather discordant. Newlands was mocked into silence by his fellow scientists; but twenty years later when the importance of his discovery was realized he was honored with the Davy Medal of the Royal Society.

**283. The Periodic System.**—Soon after the publication of the classical papers by Newlands, D. I. Mendeléeff, of Russia, and

Lothar Meyer, of Germany, independently made similar observations.

In 1869, Mendeléeff communicated a paper to the Russian Chemical Society, entitled "On the Correlation of the Properties and Atomic Weights of the Elements." In this paper he presented his conclusions as to the "dependence between the properties and analogies of the elements on the one hand and their atomic weights on the other." In 1871, Mendeléeff published his first Periodic Table, in which the elements were divided into eight groups. In arranging the elements in groups, the atomic weight was considered to be the most fundamental property of the atom. When Mendeléeff arranged the elements according to their atomic weights, a repetition of properties was observed in the periods of the elements. We have a familiar illustration of this in the halogen family:

F (19), Cl (35.46), Br (79.92), I (126.92).

Table 58 presents the Periodic Table of Mendeléeff, brought up-to-date by the inclusion of elements since discovered (such as the helium family, Group O).

**284. General Remarks on the Periodic System.**—

(*a*) At least one valence of each element corresponds to the group in which the element falls. Thus helium has a valence of zero, sodium + 1, calcium + 2, and so forth.

For non-metals two valences are usually indicated: one corresponding to the group number (*e.g.*, $Cl^{+7}$ as in $Cl_2O_7$), the other corresponding to the group number minus eight (*e.g.*, $Cl^{+7-8} = Cl^{-1}$ in HCl; $S^{+6-8} = S^{-2}$ in $H_2S$; and so forth. If an element is multivalent, its position in the periodic table indicates at least two of its valences, *e.g.*, $N^{+5}$ and $N^{-3}$, $Se^{+6}$ and $Se^{-2}$. The foregoing means that elements in the same group form analogous compounds, *e.g.* $Na_2O$, $K_2O$, $Cs_2O$; and $CaCO_3$, $SrCO_3$ and $BaCO_3$.

(*b*) Roughly speaking, metals occur on the left-hand side of the table, non-metals on the right-hand side, Table 58. Within any one group the elements in the A sub-group are more metallic than those in the B sub-group. Elements in the middle of the table tend to be amphoteric, *i.e.*, both metallic and non-metallic in behavior.

(*c*) The most active metals according to the rules in (*b*) will be found in Group I; and activity increases as we go down in the column, *i.e.*, Cs is the most active metal, reacting instantly with moisture in the air. The most active non-metal, on the other hand, will be found in Group VII (omitting Group VIII, which is a transitional group); and activity increases as we go up in this column, *i.e.*, F is the most active non-metal known.

(*d*) Mendeléeff expressed these observations in the following words:

## TABLE 58. MODIFIED MENDELÉEFF TABLE

*Periodic Table**

| Periods | | Group 0 | Group I | Group II | Group III | Group IV | Group V | Group VI | Group VII | Group VIII |
|---|---|---|---|---|---|---|---|---|---|---|
| Type of Oxide | | — | $R_2O$ | RO | $R_2O_3$ | $RO_2$ | $R_2O_5$ | $R_2O_6(RO_3)$ | $R_2O_7$ | $RO_4$ |
| Type of Hydride | | — | RH | $RH_2$ | $RH_3$ | $RH_4$ | $RH_3$ | $RH_2$ | RH | — |
| | | | A B | A B | A B | A B | A B | A B | A B | |
| First short period | | He **2**<br>4.003 | H **1**<br>1.0080<br>Li **3**<br>6.940 | Be **4**<br>9.02 | B **5**<br>10.82 | C **6**<br>12.01 | N **7**<br>14.008 | O **8**<br>16.0000 | F **9**<br>19.0 | |
| Second short period | | Ne **10**<br>20.183 | Na **11**<br>22.997 | Mg **12**<br>24.32 | Al **13**<br>26.97 | Si **14**<br>28.06 | P **15**<br>30.98 | S **16**<br>32.06 | Cl **17**<br>35.46 | |
| First long period | Even Series | A **18**<br>39.944 | K **19**<br>39.096 | Ca **20**<br>40.08 | Sc **21**<br>45.10 | Ti **22**<br>47.9 | V **23**<br>50.95 | Cr **24**<br>52.01 | Mn **25**<br>54.93 | Fe **26** Co **27** Ni **28**<br>55.85 58.94 58.69 |
| | Odd Series | | Cu **29**<br>63.57 | Zn **30**<br>65.38 | Ga **31**<br>69.72 | Ge **32**<br>72.6 | As **33**<br>74.91 | Se **34**<br>78.96 | Br **35**<br>79.92 | |
| Second long period | Even Series | Kr **36**<br>83.7 | Rb **37**<br>85.48 | Sr **38**<br>87.63 | Y **39**<br>88.92 | Zr **40**<br>91.22 | Cb **41**<br>92.91 | Mo **42**<br>95.95 | Ma **43**<br>? | Ru **44** Rh **45** Pd **46**<br>101.7 102.91 106.7 |
| | Odd Series | | Ag **47**<br>107.88 | Cd **48**<br>112.41 | In **49**<br>114.8 | Sn **50**<br>118.7 | Sb **51**<br>121.76 | Te **52**<br>127.61 | I **53**<br>126.92 | |
| Third long period | Even Series | Xe **54**<br>131.3 | Cs **55**<br>132.91 | Ba **56**<br>137.36 | La **57**<br>138.92 | Ce **58**<br>140.13 | | | | |
| | Odd Series | | | The Rare Earth Elements. Atomic Numbers **57–71** | | | | | | |
| Fourth long period | Even Series | | | | | Hf **72**<br>178.6 | Ta **73**<br>180.88 | W **74**<br>183.92 | Re **75**<br>186.31 | Os **76** Ir **77** Pt **78**<br>190.2 193.1 195.23 |
| | Odd Series | | Au **79**<br>197.2 | Hg **80**<br>200.61 | Tl **81**<br>204.39 | Pb **82**<br>207.21 | Bi **83**<br>209.0 | Po **84** | —**85** | |
| Fifth period | | Rn **86**<br>222 | —**87** | Ra **88**<br>226.05 | Ac **89** | Th **90**<br>232.12 | $UX_2$ **91** | U **92**<br>238.07 | | |

* The number in **boldface** at the right of the symbol is the Atomic Number of the element, and the number below is the International Atomic Weight for 1942.

**The properties of the elements, as well as the constitution and properties of their compounds, are periodic functions of the atomic weights of the elements.**

**285. Applications of the Periodic Law.**—Mendeléeff pointed out the following applications of the periodic system:

**(a) The classification of the elements.** Before the periodic system was developed, there was no comprehensive plan for the classification of the elements. By arranging them in groups and families the study of their physical and chemical properties is much simplified, and the memory is greatly aided.

**(b) The prediction of new elements.** Mendeléeff stated in 1869 that the discovery of many yet unknown elements might be expected, and in 1871 he actually predicted the properties of three new elements which he called *Eka-aluminum*, *Eka-boron*, and *Eka-silicon* (from the Sanskrit, *Eka*, one). In less than twenty years confirmation of Mendeléeff's bold predictions was complete. Eka-aluminum was discovered by Lecoq de Boisbaudran in 1875, and named **gallium** (Ga = 69.7); eka-boron was discovered by Nilson in 1879, and named **scandium** (Sc = 45.1) in honor of his country; eka-silicon was discovered by the German chemist Winkler in 1886, and appropriately called **germanium** (Ge = 72.6).

The striking way in which Mendeléeff's predictions were fulfilled is shown by the following illustration:

| *Eka-silicon*<br>*Predicted Properties* | *Germanium*<br>*Observed Properties* |
|---|---|
| At. wt. 72, sp. gr. 5.5. | At. wt. 72.5, sp. gr. 5.46. |
| Oxide, $EsO_2$, sp. gr. 4.7. | Oxide, $GeO_2$, sp. gr. 4.7. |
| Chloride, $EsCl_4$, liquid boiling slightly below 100°, sp. gr. 1.9. | Chloride, $GeCl_4$, liquid boiling at 86°, sp. gr. 1.887. |
| Ethide, $Es(C_2H_5)_4$, liquid boiling at 160°, sp. gr. 0.96. | Ethide, $Ge(C_2H_5)_4$, liquid boiling at 160°, sp. gr. slightly less than that of water. |
| Fluoride, $EsF_4$, not gaseous. | Fluoride, $GeF_4 \cdot 3H_2O$, white, solid mass. |

**(c) Estimation and correction of atomic weights.** Before the invention of the mass spectrograph, atomic weights were calculated from (equivalent weight times valence); but in those pioneer days it was often impossible to decide the valences of some elements. For example indium, with an equivalent weight of 38, was assumed to have a valence of 2, which would make its atomic weight $38 \times 2 = 76$. But there is already an element, arsenic, at this point in the periodic table. Chemists concluded from this that indium had, instead, a valence of 3, which gives an atomic

DIMITRI IVANOWITCH MENDELÉEFF (1834–1907)

Mendeléeff, a great teacher, writer and investigator, was born at Tobolsk, Siberia. Supported by his mother, he received an excellent education in Tobolsk and Petrograd; professor in the Technological Institute at Petrograd, followed by a professorship in the University; influential in developing Russian chemical industries; author of the Periodic System (1870); director of the Bureau of Weights and Measures.

weight of 38 × 3 = 114. This properly locates indium beneath gallium (Group III), which is like it in chemical properties.

(d) **Suggests new problems.** New elements were sought after and discovered because the periodic table predicted their existence. On the other hand, defects in the system invited research. Thus tellurium (at. wt. 127.61) should be placed after iodine (at. wt. 126.92); yet this is the wrong order from consideration of chemical properties, since iodine behaves like bromine, and tellurium like selenium. Other discrepancies are argon and potassium, cobalt and nickel. Furthermore elements within a subgroup often differ in valences: gold is $+1$ and $+3$, while copper is $+1$ and $+2$.

### CLASSIFICATION ACCORDING TO ATOMIC NUMBERS

**286. Moseley's Atomic Numbers.**—When cathode rays strike a target, X-rays are produced (Fig. 113). If the target is coated with different elements or their compounds, X-rays of slightly different wave-lengths, *i.e.*, X-ray spectra, are obtained (Fig. 114). Moseley, a brilliant young British physicist who died fighting at Gallipoli in 1915, employed the elements from aluminum to gold as targets. He found that the higher the atomic weight, the shorter the wave-length of the X-ray produced. If the consecutive numbers indicated in **bold** in Table 58 are assigned to the 92 elements, and these numbers, called **atomic numbers,** are plotted against $\sqrt{\frac{1}{\text{wave-length}}}$ of the X-rays emitted in Moseley's experiments, straight lines are obtained, (Fig. 115). $K_\alpha$ is for aluminum to silver (13 to 47), $L_\alpha$ is for zirconium to gold (numbers 40 to 79). $K_\alpha$ and $L_\alpha$ correspond to different sets of X-rays.

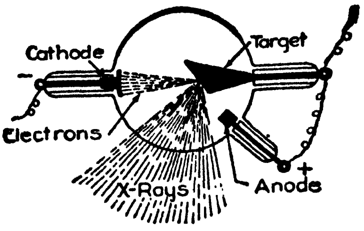


FIG. 113. X-ray tube. Moseley coated the target with different elements or their compounds.

The atomic number classification of elements is distinctly superior to that of Mendeléeff. This is immediately obvious when it is seen in Table 58 that numbers 52–53, 27–28 and 18–19 are in their correct orders, which was not the case with the atomic weights of these elements. Today our knowledge of atomic structure makes it clear why atomic numbers, not weights, are a more faithful index of chemical properties. Chemical reactions

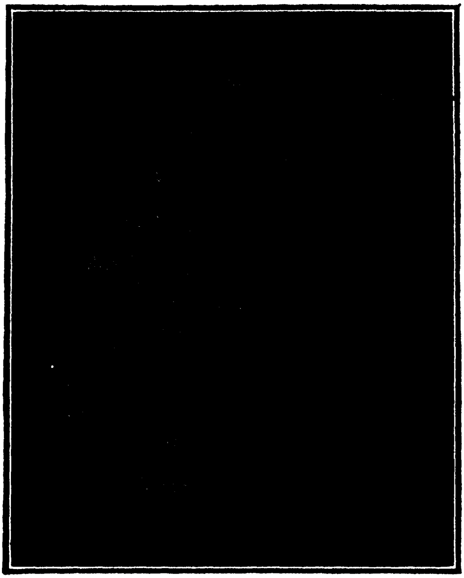


FIG. 114. X-Ray Spectra of the elements from calcium to zinc (Moseley). The spectrum of each element consists of two principal lines, but the cobalt-spectrum shows lines due to the presence of iron and nickel, the nickel appears to have contained some copper; and the brass gives two lines due to copper and two lines due to zinc. *Query:* What is the zinc spectrum?

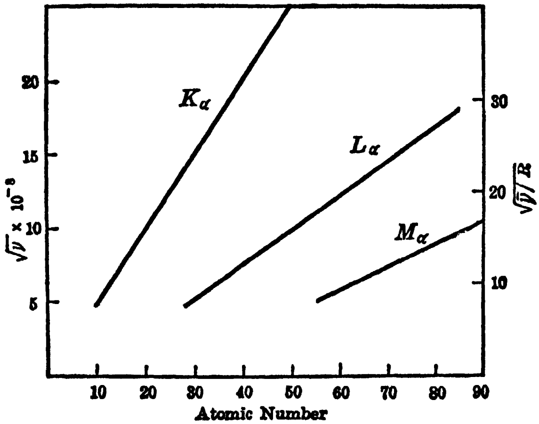


FIG. 115. Dependency of frequency of characteristic X-rays on atomic number $\left(\nu = \text{frequency} = \frac{1}{\text{wave-length}}\right)$.

are reactions between planetary electrons, which are fixed by the atomic number of the element. On the other hand, atomic weight is a statistical average of the weights of the isotopes of the element, and the weight of the nucleus does not considerably alter chemical properties.

The classification of the elements should therefore be restated as follows: **the properties of the elements are periodic functions of their ATOMIC NUMBERS.**

## QUESTION REVIEW

I. CLASSIFICATION ACCORDING TO CHEMICAL PROPERTIES.

**a. Metals and non-metals (279).**

1. Mention some general properties of metals and non-metals.

II. CLASSIFICATION ACCORDING TO ATOMIC WEIGHTS.

**a. Prout's hypothesis (280).**

2. Why was Prout's hypothesis abandoned? Was there a germ of truth in it?

**b. Döbereiner's triads (281).**

3. What two types of triads did Döbereiner discover?

**c. Newlands' octaves (282).**

4. Why did Newlands, who drew up a classification not unlike that of Mendeléeff, receive no immediate recognition?

**d. The periodic system (283).**

5. Where are the long and short periods located in the periodic table?

**(a) General remarks on the system (283, 284).**

6. Summarize the facts of valènce, chemical activity and metallic and non-metallic properties as correlated in the periodic table.

**(b) Applications of the periodic law (285).**

7. What new discoveries were the result of Mendeléeff's classification?

III. CLASSIFICATION ACCORDING TO ATOMIC NUMBERS.

**a. Moseley's atomic numbers (286).**

8. Explain in detail how atomic numbers of the elements are experimentally obtained.
9. What defects of the Mendeléeff table are rectified by the use of atomic numbers?
10. Explain in terms of atomic structure why chemical properties are indicated by atomic numbers rather than by atomic weights.

**Reading References:** Articles number 55, 403, 406, 418, 425 and 429 in the Appendix.

## CHAPTER XXIII

## THE METALLIC ELEMENTS. ALLOYS

**287. Historical.**—The metals known to the ancients were either those which occur in the free state, or which may be obtained readily by reducing their ores. They are **gold, silver, copper, lead, tin, iron and mercury.**

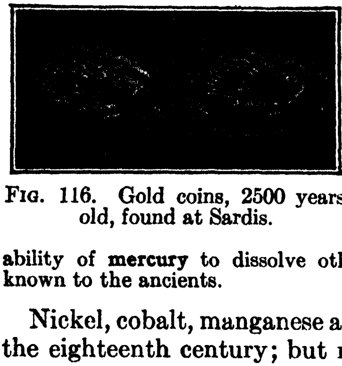


FIG. 116. Gold coins, 2500 years old, found at Sardis.

**Gold** coins nearly 2500 years old have been found in the ruins of Sardis, some of them coined during the reign of Croesus (Fig. 116). As a rule ancient gold is alloyed with **silver. Copper** dates from prehistoric times, since it occurs in the free state. A number of copper alloys were known: bronze, an alloy of copper and tin, was in use as early as 3000 B.C.; and brass, an alloy of copper and zinc, was used by the Romans. Pliny pointed out the difference between **tin** and **lead**; the latter was used by the ancient Romans for water pipes. **Iron** appeared later than copper and gold, for very little of the metal occurs in the native state. The ability of **mercury** to dissolve other metals, such as gold and silver, was known to the ancients.

Nickel, cobalt, manganese and platinum were discovered during the eighteenth century; but most of the remaining metals were first prepared during the nineteenth century.

**288. Occurrence.**—The more inactive metals occur in the free state and are called **native.** Thus gold and platinum occur largely in the native state; copper, silver, mercury, bismuth, arsenic and antimony are also found free. A majority of the metals occur only in combination with other elements. Some important minerals are given in Table 59.

**289. Metallurgy.**—**The art and science of winning the metals from their ores is called metallurgy.** An ore is a mineral from which the metal may be profitably extracted. According to this definition hematite is not usually called an iron ore unless it has as much as 50% iron in it; whereas uranite is an ore of radium if it contains as little as 0.000 001% of the valuable metal.

If the metal occurs **native** its metallurgy is quite simple. Gold for example may be **panned,** which involves the simple operation

TABLE 59. SOME IMPORTANT MINERALS

| | |
|---|---|
| *Oxides* | |
| Ferric oxide, or Hematite | $Fe_2O_3$ |
| Hydrated ferric oxide, or Limonite | $2Fe_2O_3, 3H_2O$ |
| Magnetic oxide of iron, or Magnetite | $Fe_3O_4$ |
| Stannic oxide, or Cassiterite | $SnO_2$ |
| *Sulfides* | |
| Lead sulfide, or Galena | $PbS$ |
| Zinc sulfide, or Sphaelerite | $ZnS$ |
| Cuprous sulfide, or Chalcocite | $Cu_2S$ |
| Antimony trisulfide, or Stibnite | $Sb_2S_3$ |
| *Carbonates* | |
| Ferrous carbonate, or Siderite | $FeCO_3$ |
| Zinc carbonate, or Smithsonite | $ZnCO_3$ |
| Calcium carbonate, or Calcite | $CaCO_3$ |
| Magnesium carbonate, or Magnesite | $MgCO_3$ |
| *Sulfates* | |
| Calcium sulfate, or Gypsum | $CaSO_4, 2H_2O$ |
| Strontium sulfate, or Celestite | $SrSO_4$ |
| Barium sulfate, or Barite | $BaSO_4$ |
| Magnesium sulfate, or Epsomite | $MgSO_4, 7H_2O$. |

Certain chlorides, such as NaCl, and KCl, and $MgCl_2$, are abundant; also, silicates, such as kaolin, mica and feldspar.

of washing away the earthy matter (**the gangue**), under a stream of water (placer mining). Other native ores are **smelted,** *i.e.*, melted, in a furnace. In this case a **flux,** (Latin, fluxere, *to flow*) is usually added to melt the gangue with which it forms a glass-like **slag.** This slag does not dissolve in the molten metal, but floats upon it, so that the separation of the two portions is easily achieved. Thus silica is removed from iron ore by adding limestone (lime is formed as the flux) to the furnace; a fusible slag of calcium metasilicate floats on the surface of the molten iron:

$$SiO_2 + CaO \rightarrow CaSiO_3.$$

If the metal is not in the free state, it must be treated to remove the other constituents. Oxides are smelted with reducing agents to remove the oxygen. Sulfides are heated in air, and carbonates roasted, to drive off sulfur dioxide and carbon dioxide; this usually leaves the oxide of the metal, which is then further treated with some reducing agent. Other ores require special treatments which will be taken up subsequently.

Many of these processes were known to the ancients; for example, the reduction of iron oxide with charcoal. Other important metallurgical processes were described in *de Re Metallica* of Georgius Agricola (1494–1555) translated in 1912 by the Honorable Herbert Hoover and Mrs. Hoover. Like his contemporary Paracelsus, Agricola was a physician. He was impelled to devote himself to metallurgy by the flourishing mining and smelting industry of Saxony.

**290. Concentrating the Ore.**—Many ores, especially the low-grade ores, are first treated mechanically to remove a large portion of the earthy matter, the gangue. The products of this treatment are valuable **concentrates** and ofttimes worthless **tailings.** The ore is crushed, screened and sized, and washed with water upon an inclined, vibrating table. The valuable portions of the ore and the worthless gangue settle to the bottom of the table, but at different rates, so that they are separated. Such an apparatus is called **a wet gravity concentrator.**

For several decades the **oil flotation** process has been extensively employed. Finely ground ores or tailings are agitated with water and oil. The gangue is wetted by water, and sinks into it; the valuable portion of the ore is wetted by the oil and gathers as a froth on top of the water (Fig. 117) and can be mechanically removed. Since the heavy metal-bearing portion of the ore rises against gravity this has been called *gravity concentration upside down.*

FIG. 117. Oil flotation trough. The oily particles of ore coat the air bubbles, forming a stable froth.

DEMONSTRATION 96. FLOTATION

**Materials:** Four stoppered cylinders half-full of water; carbon disulfide ($CS_2$), benzene ($C_6H_6$), $Pb_3O_4$, mineral oil, sand, powdered charcoal.

The cylinders should be made up to contain (a) water, $CS_2$ and a pinch of carbon; (b) water, $C_6H_6$ and a pinch of carbon; (c) water, sand and $Pb_3O_4$; (d) water, mineral oil, sand and $Pb_3O_4$. The carbon will separate out on the bottom ($CS_2$) layer in (a), and on the top ($C_6H_6$) layer in (b). The $Pb_3O_4$ and sand sink to the bottom in (c), whereas in (d) the $Pb_3O_4$ rises in the oil while the sand sinks to the bottom. These experiments demonstrate that the solids stay with the liquids which "wet" them, and defy the forces of gravity. This is the principle of flotation, used for separating sand and other worthless material from the valuable portion of the ore.

C. R. Hayward says:

> "At present a variety of reagents is being used which makes **differential flotation** possible; and the effect on the subsequent smelting operations has been little short of revolutionary. Not only are lead, copper, and zinc concentrates obtained nearly free from each other but each nearly free from pyrite and consequently of much higher grade."

In 1939 duPont Company marketed a series of liquids (tetrabromo-ethane, $C_2H_2Br_4$, pentachloro-ethane, $C_2HCl_5$, etc.) which are two to three times heavier than water. In this process, known as the **sink-and-float process**, a parting liquid is chosen of such density that the gangue floats and the metal-bearing particles sink.

In another mode of ore concentration, at Franklin, New Jersey, crushed ore on a moving belt passes beneath a powerful magnet; by this device magnetic oxide of iron is removed from the gangue.

**291. Reduction of oxides.** The metals whose oxides are important ores are iron, copper, manganese, tungsten, chromium, molybdenum, zinc, tin, and aluminum. All of these with the exception of aluminum (377) are reduced by the following methods.

**a. Reduction by carbon.** Coal, wood-charcoal, and coke are consumed in enormous quantities in the metallurgy of iron. Carbon monoxide is also formed in the process; it too is an important reducing agent:

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO,$$
$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2.$$

**b. Reduction by hydrogen.** Oxides of metals below zinc in the activity series (46) are reduced when heated in the presence of hydrogen. Iron of a very fine grade can be manufactured by this method:

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O.$$

**c. Reduction by aluminum.** Finely divided aluminum will reduce the oxides of most of the metals (Goldschmidt, 1903). It is particularly useful in preparing metals such as chromium and manganese for special steels, for the oxides of these metals cannot be obtained by methods (a) and (b).

$$3MnO_2 + 4Al \rightarrow 3Mn + 2Al_2O_3.$$

Since a great quantity of heat is liberated (exothermic), the process is called **aluminothermy**, and the mixture of oxide and aluminum is named **thermit**. It may be carried out in the laboratory (Demonstration 112, section 378).

**292. Roasting and Smelting.**—Carbonate ores of lead, zinc and copper are first heated to obtain oxides, and then reduced with carbon or carbon monoxide:

$$\underset{\text{malachite}}{CuCO_3, Cu(OH)_2} \rightarrow 2CuO + CO_2 + H_2O$$
$$2CuO + C \rightarrow CO_2 + 2Cu.$$

Sulfides of nickel, cobalt, antimony, copper, zinc, lead, cadmium and mercury are first roasted, and then reduced:

$$\underset{\text{zinc blende}}{2ZnS} + 3O_2 \rightarrow 2ZnO + 2SO_2$$
$$2ZnO + C \rightarrow CO_2 + 2Zn.$$

The large quantities of sulfur dioxide obtained as a by-product are used in the manufacture of sulfuric acid (578). In the case of HgS the mercury is formed directly (367).

**293. Hydrometallurgy.**—Hydrometallurgy consists in removing the metal from its ores by chemical reagents, and subsequent recovery of the metal by electrolysis or by the use of a precipitating agent in aqueous solution.

Scrap iron dumped into the wash-waters from exhausted copper mines precipitates the copper; the iron sulfate which is formed, is also sold.

$$Fe + CuSO_4 \rightarrow FeSO_4 + Cu \downarrow .$$

The important cyanide process for gold and silver consists in aerating a solution of sodium or potassium cyanide with silver or gold ore:

$$O_2 + 2H_2O + 4Ag + 8NaCN \rightarrow 4NaOH + 4NaAg\,(CN)_2,$$

followed by precipitation of the noble metal with zinc or aluminum, or by electrolysis.

**294. Electrometallurgy** is the department of metallurgy in which the electric current is employed not only for electrolytic separation or deposition of metals from solutions, but also as a source of heat (electrothermal process) in smelting, refining, annealing and welding. The use of the electric current is increasing: *e.g.*, sodium and potassium are manufactured by the electrolysis of the fused caustic alkalies, aluminum by the electrolysis of aluminum oxide dissolved in molten cryolite, and magnesium by the electrolysis of its oxide or chloride. Electrolytic zinc is produced by leaching the ore and then electrolyzing the solution, using insoluble electrodes. There has been a great advance in leaching and direct electrolytic treatment of ores.

**295. Metal Statistics.**—The world production of different metals, as estimated by the U. S. Bureau of Mines, follows. Data are for the year 1939; for those metals marked with an asterisk the latest available material was in 1938. (mt = metric tons, st = short tons, f-oz = fine ounces, t-oz = troy ounces.)

TABLE 60. WORLD PRODUCTION OF METALS

| | | | |
|---|---|---|---|
| Iron | 131,800,000 mt | *Manganese ore, about 30% Mn | 5,108,000 mt |
| | | *Chromite ore | 1,125,000 mt |
| Copper | 2,414,000 st | | |
| Lead | 1,874,000 st | | |
| Zinc | 1,645,000 mt | | |
| Aluminum | 647,400 mt | Gold | 5,922,000 f-oz |
| Tin | 162,800 mt | Silver | 5,409,000 f-oz |
| *Nickel | 127,000 mt | *Platinum | 537,000 t-oz |
| Magnesium | 32,800 mt | Mercury (1937) | 4,589 mt |
| Molybdenum | 16,500 st | | |
| Tungsten | 7,426 st | | |
| *Cobalt | 3,581 mt | | |
| Vanadium | 2,800 st | | |

**296. Physical Properties of Metals.**—In general metals exceed non-metals in luster, malleability, ductility, tenacity and conductivity. Table 61 gives some of these properties.

TABLE 61. PROPERTIES OF SOME FAMILIAR METALS

(Arranged in decreasing order)

| Malleability | Ductility | Tenacity | Conductivity |
|---|---|---|---|
| gold | gold | nickel | silver |
| silver | silver | iron | copper |
| copper | platinum | copper | gold |
| aluminum | aluminum | aluminum | aluminum |
| tin | iron | gold | zinc |
| platinum | nickel | zinc | iron |
| lead | copper | tin | nickel |
| zinc | zinc | lead | lead |
| iron | tin | | mercury |

**Luster.** Compact metals, except copper and gold, are silvery. Finely divided metals may be black, except aluminum and magnesium which may be silvery.

**Malleability and ductility.** The properties of gold are illustrated by the fact that gold has been hammered into sheets so thin that 280,000 leaves form a pile 1 inch high; that one ounce of gold can be hammered to cover 189 square feet; that gold lace is 0.000 002 mm. thick; and that 3240 meters of wire may be drawn from 1 g. of gold.

**Conductivity.** Silver is a little better than copper, 1.3 times better than aluminum, and 60 times better than mercury. Electrical conductivity runs parallel to thermal conductivity.

**Other properties** do not distinguish the metals from the nonmetals. **Densities** range from lithium which is lighter than water ($d_{Li} = 0.53$) to osmium which is 22.5 times heavier than water. On the average the members of the I-A and II-A groups of the periodic table are ten times lighter than the corresponding members of the I-B and II-B groups. **Melting points** range from −38.87° C. for mercury to 3400° C. for tungsten. Cesium and gallium have melting points near room temperature. **Hardness** varies from mercury which is liquid, through sodium and potassium which may be cut with a knife, to iridium and chromium which are hard enough to scratch glass.

**297. Alloys.**—When certain metals are melted together **alloys** are formed (Latin, *alligare*, to bind to). The alloy may be a compound of definite composition; *e.g.*, the three alloys CuMg, $Cu_2Mg$, and AlSb. In other cases the molten metals behave exactly like any two liquids, being either completely miscible (tin and lead), partially miscible (only 1.6 parts of zinc dissolve in 100 parts of lead), and immiscible (155). Upon cooling such mixtures, solid solutions are usually formed; and examination under the microscope reveals distinct particles of the two metals or of mixtures of these metals (Fig. 147). To make this solid structure more apparent, a special technique has been developed; this consists in highly polishing the surface and then etching away one species with acid. This science is called **metallography.**

The ancients realized that the addition of a foreign metal increased **hardness:** traces of arsenic are found in their copper tools, and their gold and silver coins resisted wear because they were alloyed with other metals. **Conductivity** is decreased by impurities; as little as 0.03% arsenic in copper lowers its conductivity 14%. **Malleability and melting point** are also lowered. This property is utilized in making tin-lead solders. Molten tin and lead are completely miscible, and do not form compounds. Alloys of these two metals containing 50% tin (common solder), 33⅓% tin (plumber's solder), and 64% tin (eutectic mixture) melt at 220°, 260° and 180° respectively (Fig. 118). At point *O*, the alloy freezes *en masse*, the two metals crystallizing as an intimate mixture. The figure also indicates that if the solder contains more than 36% Pb, lead will first separate out (*OB*) upon cooling the melt; if it contains less than 36% Pb, tin will separate out (*OA*).

**298. Amalgams.** When one of the metals in an alloy is mercury, the alloy is called an **amalgam** (Greek, *a soft mass*). Thus tin, zinc, gold, silver, sodium, etc., amalgamate quite readily when treated with mercury. Amalgams of iron, nickel, cobalt, manganese and platinum can be prepared by the action of sodium amalgam on salts of these metals. Amalgams are used in dental practice.

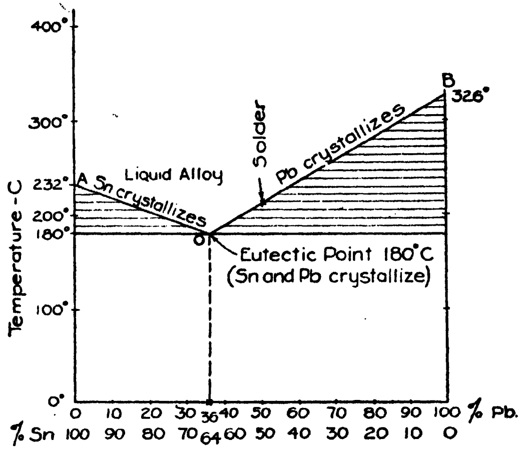


FIG. 118. Melting points of tin-lead alloys.

**299. Some Common Alloys.**—The industrial importance of alloys can hardly be exaggerated. Practically every metallic substance used in our present civilization is an alloy. Some of the principle groups of alloys follow.

**Brasses.**—Alloys of copper and zinc.

**Bronzes.**—Essentially alloys of copper and tin; they may also contain zinc and lead.

**Machinery Brasses and Bronzes.**—Alloys of copper, tin, zinc and sometimes other metals.

**White Bearing Metal Alloys.**—Alloys of tin, antimony and copper.

**Soft Alloys** (solder, type metal, etc.).—Alloys of lead and tin; or of lead, antimony, and tin.

**Aluminum Alloys.**—Aluminum bronze (Cu 90–95); duralumin.

**Nickel Alloys.**—German silvers (Ni, Zn, Cu); nichrome; monel metal.

**Fusible Alloys.**—Wood's metal; Rose's metal (melt in boiling water).

**Alloys of the Precious Metals.**—White gold, osiridium, etc.

**Amalgams.**—Alloys containing mercury.

**Alloys of Iron and Steel.**—Carbon steels, tungsten steels, etc.

## QUESTION REVIEW

I. HISTORICAL (287).

1. What metals were known to the ancients, and to what uses were they put? How can chemical analysis date an ancient coin? Why did the iron age follow the bronze age?

II. OCCURRENCE (288).

2. Name and give the formulas for an oxide, a sulfide, a carbonate and a sulfate mineral.

III. METALLURGY (289).

**a. Survey of processes.**

3. Define metallurgy, slag, flux, gangue, native ore, smelting, roasting, differential flotation, parting liquid, panning, placer mining, tailings, concentrates.
4. Outline the principle involved in treating native ores; also oxide, carbonate and sulfide ores.

**b. Concentrating the ore** (290).

5. Describe wet gravity concentration; oil flotation; the sink-and-float process.

**c. Reduction of oxides** (291).

6. Illustrate by means of equations three reducing agents used in metallurgy. Why could not sodium be prepared by the reduction of NaCl with hydrogen?

**d. Roasting and smelting** (292).

**e. Hydrometallurgy** (293).

**f. Electrometallurgy** (294).

7. Give one process, with equations, illustrating each of these branches of metallurgy.

**g. Metal statistics** (295).

8. Arrange the following metals in order of decreasing tonnage production: vanadium, magnesium, iron, lead, copper, tin, nickel, gold, mercury, zinc, aluminum.

IV. PHYSICAL PROPERTIES OF METALS (296).

9. Arrange the following metals in order of decreasing malleability and conductivity: iron, gold, tin, silver, copper.
10. Give examples illustrating the extremes of density, melting point and hardness among the metals.

V. ALLOYS (297).

**a. Alloys.**

11. Give examples showing that two metals when melted together behave like any two liquids.
12. Illustrate how the physical properties of a metal may be changed by adding a second metal to it. For what use must copper be especially pure?

**b. Amalgams** (298).

13. What metals will not alloy directly with mercury? How is an amalgam of these metals made?

**c. Some common alloys** (299).

14. Name the metals present in three groups of alloys.

**Reading References:** Articles in the Appendix:

*Alloys:* 11, 40, 49, 218, 228 and 337.

*Metal statistics:* 37, 40, 49, 142, 145, 151, 212, 248, 340, 420 and 429.

*Metallurgy:* 61, 306 and 332. For the metallurgy of individual elements (*e.g.*, Cu, Ni, Fe) see reading references at the end of each chapter.

# CHAPTER XXIV

## THE ALKALI METALS: GROUP I-A

**300. Metals of the Alkali Family.**—The members of this family are given in Table 62.

TABLE 62. THE ALKALI METALS

| Element | Atomic Weight | Atomic Number | Electronic Structure | Density (Solid) | Melting Point | Boiling Point |
|---|---|---|---|---|---|---|
| Lithium, Li | 6.94 | 3 | 2–1 | 0.53 | 186.0° | 1336° |
| Sodium, Na | 23.00 | 11 | 2–8–1 | 0.97 | 97.5° | 880° |
| Potassium, K | 39.10 | 19 | 2–8–8–1 | 0.86 | 62.3° | 760° |
| Rubidium, Rb | 85.48 | 37 | 2–8–18–8–1 | 1.53 | 38.4° | 700° |
| Cesium, Cs | 132.91 | 55 | 2–8–18–18–8–1 | 1.87 | 28.5° | 670° |

**Their occurrence and preparation** has already been discussed (125–130; 139–141).

In general, the alkali metals may be prepared by the electrolysis of the fused hydroxide or chloride, or by the interaction of the carbonate (except lithium) with carbon at a high temperature.

DEMONSTRATION 97. ALKALI METAL PROPERTIES

**Materials:** Lump of sodium, sodium wire, other alkali metals, three 100 cc. crystallizing dishes containing water, two leads from a doorbell and dry cell, knife, photoelectric cell in operation, sodium hydroxide, calcium hydroxide, 2 test-tubes over burner.

The properties which follow may be demonstrated. **Physical properties** of the alkali metals are in general alike, although in some respects sodium and lithium differ. Lithium occasionally resembles the alkaline earth metals. The alkali metals are all very soft, malleable, and light in weight, three of them being light enough to float upon water. When freshly cut they are silvery white. They conduct electricity. As a rule compounds of this family are readily soluble in water.

DEMONSTRATION 98. FLAME TESTS FOR GROUP I-A

**Materials:** Three salt shakers holding LiCl, NaCl and KCl respectively; cigarette, platinum wire, burner, HCl in test-tube, solutions of alkali metal salts, cobalt-blue glass, spectroscope.

Salts of the alkali metals impart characteristic colors to the non-luminous flame: lithium, red; sodium, yellow; and potassium, violet as observed through the cobalt-blue glass. Potassium and lithium flames are obtained when a cigarette is held in the flame. If a wire is used for the testing, it is cleaned by dipping in acid periodically.

**Chemical properties** of the alkali metals are similar, and are associated with the important fact that the outermost electron in all of them is an $s^1$ electron. They have a great tendency to lose this electron to form an ion:

$$M \rightarrow M^+ + e,$$

and for this reason all of them exhibit a marked photoelectric effect, giving off electrons when light is shone upon them. This same property is related to their chemical reactivity, which increases with increase in atomic weight. These metals quickly tarnish, therefore, when exposed to the air; and they all interact vigorously with cold water to form a hydroxide and free hydrogen:

$$2M + 2HOH \rightarrow 2M(OH) + H_2 \uparrow.$$

With potassium, rubidium, and cesium the action is so violent that the hydrogen ignites spontaneously. When the alkali metals are heated with hydrogen they unite to form hydrides. (*e.g.*, sodium hydride, $NaH$.)

**Compounds** of the alkali metals are not appreciably hydrolyzed in water. These compounds are usually completely ionized, *i.e.*, they are salts. The hydroxides of these metals are very active, and dissolve in, or react with, water and acids with the evolution of great heat. Also these hydroxides can be subjected to a very high temperature without the loss of water; whereas the hydroxides of other metals (*viz.*, $Ca(OH)_2$) lose water quite readily when heated, yielding the corresponding oxides. Neither are their carbonates or their nitrates decomposed upon heating, with the exception of the lithium salts.

The hypothetical metal, **ammonium** ($NH_4$), has never been prepared, but it forms a series of compounds which are analogous to those of the alkali metals.

## LITHIUM $^{6.94}_{3}Li$

**301. Lithium.**—Lithium owes its name to a Greek word meaning *stony*, for at the time of its discovery it was believed that it occurred only in the mineral kingdom. It is widely distributed and occurs in quantity in a few minerals, such as petalite and lepidolite. Its salts also occur in certain mineral springs and in the soil, being taken up by such plants as the beet and tobacco. Lithium compounds were recognized by Arfvedson in 1817, but the element was first isolated in quantity by Bunsen in 1858.

Lithium can be prepared by the electrolysis of its fused chloride; but it is better to employ a mixture of the bromide and chloride, because such a mixture has a lower melting point than has the pure chloride.

Lithium is the lightest solid known (except solidified hydrogen). The metal is softer than lead, but harder than the other metals of the alkali group. Its chemical properties are similar to those of sodium and potassium, but it is less active. The carbonate ($Li_2CO_3$) and the phosphate ($Li_3PO_4$, $2H_2O$), unlike the corresponding compounds of the other alkali metals, are sparingly soluble in water.

Lithium compounds impart a bright red color to the non-luminous flame, and the spectrum of lithium consists of a prominent crimson line and a feebler orange line.

About 1000 tons of lithium compounds were produced in 1940 in the United States. The chief consumer of lithium compounds is the glass industry, which employs it as a flux, and in increasing the electrical insulating properties of the glass, and in increasing ultra-violet transmission. Lithium compounds also improve the gloss of enamels. Single crystals of lithium fluoride weighing 2200 g. have been prepared as a substitute for natural calcium fluoride in making prisms.

## SODIUM $^{22.997}_{11}Na$

**302. Sodium.**—We have already discussed (125) the occurrence of sodium as sodium chloride, the manufacture of sodium hydroxide by the electrolysis of brine or of molten sodium chloride, and the properties and uses of these substances.

**303. Sodium Carbonate, $Na_2CO_3$.**—Sodium carbonate occurs in nature in large quantities. In Nevada and in California it is found in alkaline lake waters and as incrustations, due to deficient rainfall and evaporation. The deposits of "natural soda" in our western states have been worked commercially in a number of places. There are also large foreign deposits of natural soda.

Thus, in British East Africa there is a deposit which is estimated to contain at least 200,000,000 tons. This natural product is called "trona" and it has the formula $Na_2CO_3$, $NaHCO_3$, $2H_2O$. Until the end of the eighteenth century, soda was obtained exclusively from the ash of seaweed, which meant more expensive soap and glass. This source of the carbonate no doubt explains the origin of the name "soda ash."

Chief process for the manufacture of this key product is the **Solvay Ammonia Process.** The reactions upon which the process is based were known as early as 1852, but the mechanical details for the commercial production of the compound were not perfected until the latter part of the sixties. This we owe to the Belgian chemists, Ernest and Alfred Solvay.

**Brine is saturated with ammonia and then treated with carbon dioxide,** in consequence of which sodium bicarbonate separates out:

$$NaCl + H_2O + NH_3 + CO_2 \rightleftarrows NaHCO_3 \downarrow + NH_4Cl;$$
$$\text{or, } NaCl + NH_4HCO_3 \rightleftarrows NaHCO_3 \downarrow + NH_4Cl.$$

The reactions are really ionic, the bicarbonate ion (from $NH_4HCO_3$) combining with the sodium ion to form sodium bicarbonate·

$$Na^+ + HCO_3^- \rightarrow NaHCO_3 \downarrow.$$

**The bicarbonate is heated to obtain sodium carbonate,** and carbon dioxide passes off to be used again in the first step:

$$2NaHCO_3 \xrightarrow{\text{heat}} Na_2CO_3 + H_2O + CO_2.$$

The mechanical details of the first step follow. Ammoniacal brine is delivered to a "carbonating tower," which is divided by a number of perforated partitions (Fig. 119). The carbon dioxide enters under the lowest dome, and rises in small bubbles through the perforations. A thick, milky liquid, containing $NaHCO_3$ in suspension and $NH_4Cl$ and NaCl in solution, is drawn off at the bottom, the bicarbonate removed by filtration, and the filtrate is then treated with lime to recover ammonia, calcium chloride being obtained in large amount as a by-product.

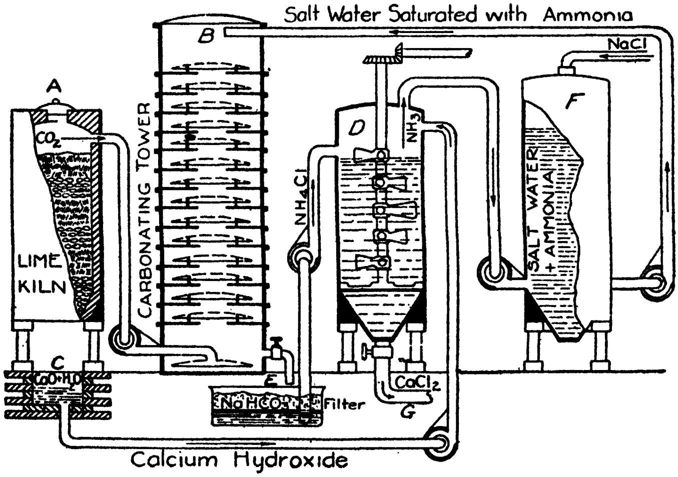


FIG. 119. The Solvay process for soda.

DEMONSTRATION 99. THE SOLVAY PROCESS

Materials: Stoppered wide-mouth 200 cc. bottle, concentrated ammonium hydroxide, solid sodium chloride, lump of dry-ice.

A saturated solution of sodium chloride in ammonium hydroxide is made. Lumps of dry-ice are then dropped in. In half an hour an abundant yield of sodium bicarbonate settles to the bottom of the bottle. This illustrates the reaction in the first step of the Solvay process.

Sodium carbonate is very soluble in water, and its aqueous solution has a strongly alkaline reaction (explain). The decahydrate, $Na_2CO_3, 10H_2O$, is commonly known as "washing soda" or "sal soda"; it consists of large monoclinic crystals. Sodium carbonate is used on a large scale for the manufacture of glass, caustic soda, soap, sodium bicarbonate, and paper and pulp, also in the softening of water, etc.

Production of sodium carbonate in the United States in 1940 amounted to approximately 3,000,000 tons. 100,000 tons of this was from the natural deposits at Searles Lake, California and neighboring localities.

**304. Other Process for Sodium Carbonate.**—An **electrolytic** method for preparing sodium carbonate is finding special favor in Japan. By electrolysis of salt, sodium hydroxide is formed; and this reacts with excess carbon dioxide to form sodium carbonate:

$$NaCl \xrightarrow{\text{electrolysis}} NaOH \xrightarrow{+CO_2} Na_2CO_3.$$

Still a third process, the **LeBlanc Soda Process,** was an important milestone in the progress of industrial chemistry. LeBlanc invented his process to break the British monopoly on sodium carbonate during the Napoleonic Wars. Cheap soda was the immediate outcome. Cheap soda brought cheap glass and cheap soap, and directed attention to personal hygiene. The steps in the LeBlanc process are:

$$NaCl \xrightarrow[\text{heat in pan}]{H_2SO_4} NaHSO_4 \xrightarrow[\text{furnace}]{NaCl} \underbrace{Na_2SO_4 \xrightarrow{C} Na_2S \xrightarrow{CaCO_3} Na_2CO_3}_{\text{coal+limestone in furnace}}.$$

The product $Na_2SO_4$ is known as **salt cake.** A considerable increase in demand for salt cake during the past decade has kept the LeBlanc process alive on the European Continent and in England.

**305. Sodium Bicarbonate, $NaHCO_3$.**—Sodium bicarbonate, sodium hydrogen carbonate, or baking soda, is prepared (a) in the first step of the Solvay process or (b) by the electrolytic process (304), or (c) by treating the decahydrate with carbon dioxide:

$$Na_2CO_3{,}10H_2O + CO_2 \rightarrow 2NaHCO_3 + 9H_2O.$$

### DEMONSTRATION 100. BAKING POWDERS

**Materials:** Test glass, cream of tartar, sodium bicarbonate (or baking powder).

**Baking powders** contain sodium bicarbonate and some acidic substance; and in addition, starch or flour to prevent the two from interacting until water has been added. Acidic substances used are cream of tartar (potassium bitartrate, $KHC_4H_4O_6$), or primary phosphates ($NaH_2PO_4$ or $Ca(H_2PO_4)_2$). Sour milk is also added by the housewife for the same purpose, the acid in the milk reacting with the sodium bicarbonate to liberate carbon dioxide. The carbon dioxide passes up through the dough and causes it to rise.

$$NaHCO_3 + \underset{\substack{\text{cream of}\\\text{tartar}}}{KHC_4H_4O_6} \rightarrow H_2O + \underset{\substack{\text{Rochelle}\\\text{salt}}}{KNaC_4H_4O_6} + CO_2\uparrow.$$

**306. Analytical.**—Virtually all sodium compounds are soluble in water. Sodium fluorosilicate, $Na_2SiF_6$, and sodium hydrogen pyroantimonate, $Na_2H_2Sb_2O_7$, are the least soluble. The sodium-ion, $Na^+$, is colorless. The gas flame is colored yellow by all sodium compounds. Since the flame test is a very delicate one and sodium compounds are widely distributed, great care has to be exercised in testing for sodium.

### POTASSIUM $^{39.1}_{19}K$

**307. Occurrence.**—Potassium compounds are widely distributed, constituting 2.6% of the earth's crust. The presence of potash in clay is accounted for by the weathering of potash feldspars, such as orthoclase, $KAlSi_3O_8$:

$$\underset{\text{orthoclase}}{2KAlSi_3O_8} + 2H_2O + CO_2 \rightarrow \underset{\substack{\text{kaolin}\\\text{(clay)}}}{H_4Al_2Si_2O_9} + \underset{\text{quartz}}{4SiO_2} + \underset{\text{potash}}{K_2CO_3}.$$

The potash is soluble, and finds its way into the soil and waters of the earth.

Salt deposits of sylvite (KCl), carnallite (KCl, $MgCl_2$, $6H_2O$), etc. in the Stassfurt mines in Germany will supply the world with potash fertilizers for the next thousand years (Fig. 120) Alsace and Poland, also, have enormous deposits. At the time of the first World War, the United States was wholly dependent upon these European sources, but has since become self-sufficient.

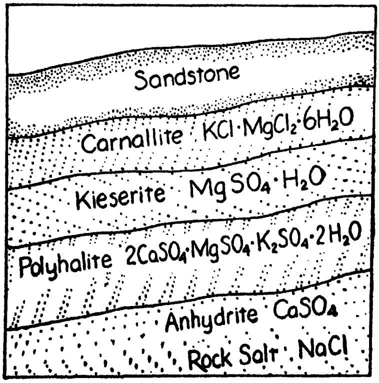


FIG. 120. Stassfurt salt deposits.

The 1938 production of potash from the brines of Searles Lake, California, and from the sylvite of New Mexico, where the mines are 1000 feet underground, accounted for 98% of the domestic production. World production for 1937 was 3,100,000 metric tons, calculated as $K_2O$, with Germany accounting for 63.4%, France 15.7%, Russia 8.5%, U. S. A. 8.3%, Poland 3.4%, Palestine 0.5%, and other countries 0.2%. It will be noted that potash production figures are always calculated on the basis of $K_2O$. The term *potash* is thus applied not only to potassium carbonate, $K_2CO_3$, but in a looser sense to KOH, and in the fertilizer industry to $K_2O$. Of the 467,000 tons of potash sold in the United States in 1938, 94% was destined for mixed fertilizers.

**308. Preparation and Properties.**—The methods used for the preparation of the metal are the same as those used for sodium. As the metal has no particular use, very little of it is produced. Potassium was first prepared by Davy, in 1807, by the electrolysis of fused potassium hydroxide.

He placed some caustic potash in a silver dish, heated it to fusion, and then passed an electric current through the molten mass, the dish serving as a cathode. Much to his surprise, he observed the formation of silvery globules, which ignited spontaneously. Davy was so excited that "he began to dance and it was some time before he could control himself to continue his experiments."

Potassium is a soft metal, possessing a silvery luster. Its chemical properties are similar to those of sodium, but it is more active. Thus, when potassium is brought in contact with cold water, so much heat is generated that the liberated hydrogen ignites, and burns with a violet flame, due to the vapor of the metal.

**309. Potassium Compounds.**—In general, sodium salts are cheaper than potassium salts, and have replaced them in industry, *i.e.*, NaCN for electroplating, and $Na_2Cr_2O_7$ for oxidizing. However, potassium compounds (*e.g.*, $KNO_3$, $K_2Cr_2O_7$) are usually not deliquescent, whereas the corresponding sodium salts are; for this reason the potassium salt, although more expensive, must sometimes be employed (*e.g.*, in fireworks). In the glass industry, soda glass is soft; potash glass is hard. In the soap industry, sodium soaps are hard soaps, whereas potassium soaps are soft pastes.

A few important potassium compounds follow.

**Potassium Chloride, KCl.**—This salt occurs in large quantities in nature, especially in the salt deposits of Stassfurt and of Alsace. **Sylvite** is nearly pure potassium chloride, and **carnallite** is a double chloride, KCl, $MgCl_2$, $6H_2O$. Potassium chloride is also produced from kelp, brine, etc. The properties of the salt are quite similar to those of sodium chloride. It is used very extensively as a fertilizer and as the source of other potassium compounds.

**Potassium Hydroxide, KOH.**—Caustic potash is manufactured by the methods used in the production of sodium hydroxide. The two compounds have similar properties, but for commercial purposes the cheaper sodium compound is generally used. It is utilized in the manufacture of soft and liquid soaps and for absorbing carbon dioxide.

**Potassium Nitrate, $KNO_3$.**—This salt is commonly termed **saltpeter** or **niter.** It occurs in the surface soils in the vicinity of certain Oriental villages and cities. Potassium nitrate is manufactured by boiling together concentrated solutions of Chile saltpeter ($NaNO_3$) and potassium chloride. These salts interact by double decomposition and the less soluble sodium compound is precipitated. Since the sodium nitrate is deliquescent, it cannot be used in fireworks, and potassium nitrate is substituted. $KNO_3$ is an active oxidizing agent, is not deliquescent, and is used in matches, pyrotechnics, detonators, and percussion caps.

**310. Analytical.**—Nearly all potassium compounds are soluble in water. Potassium may be precipitated, however, as potassium bitartrate, $KHC_4H_4O_6$, and as potassium chloroplatinate, $K_2PtCl_6$ (yellow crystals). The latter compound is much less soluble in alcohol. Other sparingly soluble salts are the perchlorate ($KClO_4$) and the fluosilicate ($K_2SiF_6$). The potassium ion, $K^+$, is colorless.

Potassium salts impart a violet color to the non-luminous flame; this is observed through a cobalt-blue glass, which screens out the yellow sodium flame usually accompanying the potassium.

### RUBIDIUM, CESIUM AND AMMONIUM

**311. Rubidium and Cesium.**—Soon after the invention of the spectroscope, Bunsen announced, in 1860, the discovery of cesium, a new alkali metal; and in 1861 he also discovered by means of spectrum analysis a second alkali metal, which he named rubidium. Bunsen discovered these metals in the waters of Durkheim and in the mineral petalite. They are rare elements, and are very similar to potassium in most respects, but are more electropositive.

In general, their salts are similar to those of the other alkali metals, particularly potassium. The element *cesium* (Latin *caesius*, bluish-gray) owes its name to the fact that it gives blue lines in its spectrum, and *rubidium* (Latin *rubidus*, red) owes its name to the red lines.

**312. Ammonium, $NH_4$.**—The name **ammonium** is applied to the metallic radical, $NH_4$, which has never been obtained in the free state. It is probable, however, that a solution of ammonium in mercury (ammonium amalgam) can be obtained by the electrolysis of an ammonium salt (*e.g.*, $NH_4Cl$) with a pool of mercury as cathode, or by placing sodium amalgam in a strong solution of the salt.

Ammonium salts are similar to the alkali metals, particularly rubidium, as regards solubility and crystal form. The salts may be prepared by treating ammonia, or ammonium hydroxide, with acids:

$$NH_4OH + HNO_3 \rightarrow NH_4NO_3 + H_2O.$$

Ammonium salts often sublime; thus ammonium chloride volatilizes when a mixture of chlorides of sodium, potassium and ammonium is heated.

**Analytical** detection of the ammonium radical involves heating the ammonium salt with sodium hydroxide; ammonia gas is evolved and may be smelled:

$$NH_4X + NaOH \rightarrow NaX + NH_3 \uparrow + H_2O.$$

The ammonium radical is colorless. Like potassium salts, ammonium salts are very soluble, with the exception of sparingly soluble bitartrate ($NH_4HC_4H_4O_6$) and chloroplatinate ($(NH_4)_2PtCl_6$).

**Ammonium nitrate** $NH_4NO_3$ is an important explosive and fertilizer (512). **Ammonium sulfide** $(NH_4)_2S$ is formed in solution by the reaction:

$$2NH_4OH + H_2S \rightarrow (NH_4)_2S + 2H_2O,$$

which hydrolyzes to form $NH_4HS$ in excess of $H_2S$. These compounds are important in routine chemical analysis with sulfides (577).

**313. Group I-A Compounds.**—A summary of properties is given in Table 63.

TABLE 63. GROUP I-A: USES

| | |
|---|---|
| **Ammonium and its compounds** | **$NH_4^+$, amalgam (312), $NH_3$, $(NH_4)_2SO_4$, $NH_4NO_3$ (512) as fertilizers and explosives.** |
| Ammonium chloride<br>sal ammoniac, $NH_4Cl$ | soldering flux; dry cells; textile printing; medicine; fertilizer. |
| Ammonium phosphates | primary and secondary salts (548) are fertilizers and textile-fireproofing agents. |
| **Lithium and its compounds** | **Li compounds in glass, lithium fluoride (301).** |
| Lithium chloride<br>$LiCl$ | mineral waters; pharmaceuticals; deep red color for pyrotechnics. |
| **Potassium and its compounds** | **ore, potash (307); K (308); KCl, KOH, $KNO_3$ (309); bitartrate, chloroplatinate, perchlorate (310).** |
| Potassium bitartrate<br>$KHC_4H_4O_6$ | from wine lees (bottom of cask) and argol (crystals on side of cask); baking powders; candy; tartrates. |

TABLE 63—*continued*

| | |
|---|---|
| Potassium carbonate<br>pearl ash, $K_2CO_3$ | soft soap; hard glass; potassium compounds, textiles. |
| Potassium chlorate<br>$KClO_3$ | active oxidizing agent in pyrotechnics, matches, explosives; also in medicine. |
| Potassium chromate | mordant for dyestuffs; leather. |
| Potassium ferricyanide<br>red potassium prussiate<br>$K_3Fe(CN)_6$ | blue-print paper; printing wool and cotton; non-poisonous. |
| Potassium ferrocyanide<br>yellow pot. prussiate<br>$K_4Fe(CN)_6, 3H_2O$ | non-poisonous medicine; engraving. |
| Potassium iodide, KI<br>and the bromide, KBr | photographic emulsions; medicine. |
| Potassium permanganate<br>$KMnO_4$ | deep purple water-soluble crystals; oxidizing agent in bleaching, dyeing shoe leather, darkening wood; disinfectant; treating poison ivy. |
| Potassium sodium tartrate, Rochelle salt<br>$KNaC_4H_4O_6, 4H_2O$ | very soluble; medicine; reduces silver solutions in making mirrors. |
| Potassium sulfate<br>$K_2SO_4$ | fertilizer; for potash alums see 381. |
| **Sodium and its compounds** | **Na (126–130); NaCl (125); NaOH (139–140); $Na_2CO_3$ (303); $Na_2SO_4$ (304); baking powder, $NaHCO_3$ (305).** |
| Sodium cyanide<br>NaCN | very poisonous; extracting gold and silver; electroplating; $NaCl + Na_2CO_3 + NaCN$ for case-hardening steel. |
| Sodium dichromate<br>$Na_2Cr_2O_7, 2H_2O$ | cheap, powerful oxidizing agent for bleaching dyes and oils; manufacturing chromium salts. |
| Sodium hydrosulfite<br>sodium hyposulfite<br>$Na_2S_2O_4, 2H_2O$ | powerful reducing agent used in textile dyeing. |
| Sodium lauryl sulfate<br>$NaSO_3C_{11}H_{23}$ | soapless soap; a sodium alkyl sulfate; introduced in 1930; Ca and Mg salts are soluble and therefore lather with seawater and form no scum. |
| Sodium nitrate<br>$NaNO_3$ | Chile saltpeter, most abundant natural nitrate; fertilizers and explosives (512). |
| Sodium nitrite<br>$NaNO_2$ | deliquescent; supplies $-NO_2$ (nitro) group to dyes. |
| Sodium peroxide<br>$Na_2O_2$ | from burning Na in excess air; oxidizing agent for syntheses and bleaching. |
| Sodium phosphate<br>$Na_2HPO_4, 12H_2O$ | baking powder (305); medicines; textiles, a water softener. |
| Sodium silicates<br>$Na_2SiO_3, SiO_2$ to<br>$Na_2SiO_3, 3SiO_2$ is<br>water glass | binder; heat-resisting cement; 15–50% added as filler to soaps; preserving eggs.<br>Sodium metasilicate and sodium hexametaphosphates are detergents for softening water. |

TABLE 63—*continued*

| | |
|---|---|
| Sodium sulfide<br>$Na_2S$ | deliquescent crystals; powerful reducing agent for dyes; removes hair from hides; sulfurizing lead and copper ores for flotation. |
| Sodium sulfate<br>$Na_2SO_4$<br>Glauber's salt<br>$Na_2SO_4, 10H_2O$ | evaporation of water solution gives $Na_2SO_4$ above, and $Na_2SO_4, 10H_2O$ below, 32.4° C.; glass; paper-pulp, dyeing, tanning; in mineral water has same effect as Epsom salts; 80,000 tons in U. S. A. in 1938. |
| Sodium tetraborate<br>$Na_2B_4O_7, 10H_2O$<br>kernite<br>$Na_2B_4O_7, 4H_2O$ | 219,513 tons of borates produced in U. S. in 1938; water solutions give decahydrate ($10H_2O$) below, pentahydrate ($5H_2O$) above, 60° C.; pyrex glass; washing powders. |
| Sodium thiosulfate<br>$Na_2S_2O_3, 5H_2O$ | photographers' "hypo," large crystals; dissolves AgBr from photographic plate, leaving the silver negative (328); removes Cl from bleached fabrics. |
| **Rubidium and Cesium** | **311.** |

## QUESTION REVIEW

**Metals of the alkali family (300).**

1. Compare the alkali metals as regards (*a*) relative boiling points, densities, and melting points; (*b*) chemical reactivity; (*c*) solubility of their compounds; (*d*) flame tests.

I. LITHIUM (301).

2. What is the chief industrial use for lithium?

II. SODIUM (302).

**a. Sodium. Sodium chloride. Sodium hydroxide (125–30; 139–41; 148).**

3. Outline (*a*) the occurrence of sodium chloride; (*b*) methods for preparing sodium hydroxide; (*c*) preparation of sodium; (*d*) general properties of these substances.

**b. Sodium carbonate (303–4).**

4. Describe the Solvay process in detail. How may the process be demonstrated?
5. What two other sources of sodium carbonate are there?

**c. Sodium bicarbonate (305).**

6. Explain the composition of baking powder, and account for its action.

**d. Analytical (306).**

III. POTASSIUM (307).

**a. Occurrence (307).**

7. Account for the presence of potash in the soil.
8. Which are the great potash-producing countries? To what use is the potash put?

**b. Preparation and properties (308).**

9. Why was potassium not prepared during the Middle Ages? Outline its properties.

**c. Potassium compounds (309).**

10. Contrast the industrial applications of compounds of sodium with those of potassium.

**d. Analytical (310).**

IV. RUBIDIUM AND CESIUM (311).

11. In what way do their names indicate how these elements were discovered?

V. AMMONIUM (312).

12. How would you identify the presence of the ammonium radical in an unknown salt?
13. State some properties of ammonium compounds.

**Review of compounds in group I-A** (313).

14. Memorize ten compounds and their uses (Table 63).

**Reading References:** Articles in the Appendix:

*General:* 61 and 218.
*Potash fertilizer:* 35, 206, 213, 230, 243 and 252.
*Sodium and its compounds:* 133, 207, 216 and 252.

# CHAPTER XXV

## THE COPPER GROUP

**314. Copper, Silver, and Gold : Group I-B.**—These three metals are known as the coinage metals because they are extensively used in coinage. Their properties are given in Table 64.

TABLE 64. THE COPPER GROUP

| Element | Atomic Weight | Atomic Number | Electronic Structure | Density | Melting Point | Boiling Point |
|---|---|---|---|---|---|---|
| Copper, Cu | 63.57 | 29 | 2–8–18–1 | 8.94 | 1083° | 2310° |
| Silver, Ag | 107.88 | 47 | 2–8–18–18–1 | 10.5 | 960.5° | 1950° |
| Gold, Au | 197.2 | 79 | 2–8–18–32–18–1 | 19.3 | 1063° | 2600° |

The metals of the copper group are malleable and ductile and are excellent conductors of heat and electricity. Group 1-B differs in many respects from group I-A; many of these differences may be interpreted in terms of their atomic structure. Some of these differences are tabulated in Table 65. An atom of group I-B is very compact, since movement of the outermost electron is restrained by the 18-electron sub-shell, in contrast with the 8-electron sub-shell for the alkali metals. As a result of this small atomic volume, the coinage metals are more dense. Also, being more closely packed, it is more difficult to pull their atoms apart, *i.e.*, their boiling points are higher than those of the alkali metals. The formation of $Cu^{+2}$ and $Au^{+3}$, as well as the univalent ions, is attributed to the possibility of removing 2 or 3 electrons from the 18 sub-shell. The extra electrons in the sub-shell also makes it possible for the formation of complex ions such as $Cu(NH_3)_4^{++}$, $Ag(NH_3)_2^+$, and $(AuCl_4)^-$, a property not exhibited by the alkali metals.

The oxides and hydroxides of the alkali metals are strongly basic, while those of the Copper Group (except $Ag_2O$) are feebly so. The alkali metals are exceedingly active, while the other metals are among the most inactive of the metals, all being found native and only copper being oxidized in the air.

TABLE 65. CONTRAST OF GROUPS I-A, II-A WITH GROUPS I-B, II-B

| A GROUPS | B GROUPS |
|---|---|
| I-A. Alkali metals: Li, Na, K, Rb, Cs | I-B. Cu, Ag, Au |
| II-A. Alkaline earth metals: (Be), Mg, Ca, Sr, Ba, Ra | II-B. Zn, Cd, Hg |
| **Large atoms** | **Small atoms** |
| K is 2–8–8–1 | Cu is 2–8–18–1 |
| Outermost electron in large orbit, giving a large atom. | Outermost electron held in by 18-electron shell, giving a small atom. |
| Ca is 2–8–8–2 | Zn is 2–8–18–2 |

From this follows:

| | |
|---|---|
| Compressible | Not very compressible |
| Low density | Heavy metals |
| alkalies ½ to 2 | Cu 9 to Au 19 |
| alk. earths 1 to 3½ | Zn 7 to Hg 14 |
| Most active metals | Least active metals |
| heaviest most active | heaviest least active |
| oxidize in air | not oxidize in air |
| recently discovered | earliest used metals |
| strong bases | weak bases |
| salts ionize | salts hydrolyze |
| One valence only | Variable valence |
| alkali metals +1 | Cu +1 and +2; Au +1 and +3 |
| alk. earth metals +2 | Hg +1 and +2 |
| Simple cations only | Complex anions |
| $Na^+$, $Ca^{++}$, *etc.* | $(AuCl_4)^-$; $(ZnO_2)^=$, *etc.* |
| | Complex cations |
| | $Cu(NH_3)_4^{++}$; $Ag(NH_3)_2^+$, *etc.* |

Gold and silver and the metals of the Platinum Group are called the "noble metals," the "noble" character of the element in the group increasing with increasing atomic weight. Being quite inactive, the metals of the Copper Group occur in the free state, and have but little tendency to form ions.

**315. Production Statistics.**—

TABLE 66. ESTIMATED WORLD PRODUCTION OF METALS IN GROUP I-B

| REGIONS | COPPER MINED short tons (1939) | SILVER fine oz. (1939) | GOLD fine oz. (1939) |
|---|---|---|---|
| Africa | 393,442 | 5,409,000 | 15,483,000 |
| Asia | 146,882 | 21,843,000 | 3,545,000 |
| Australia | 26,000 | 15,466,000 | 2,197,000 |
| Europe | 281,344 | 23,430,000 | 5,922,000 |
| North America | 1,120,096 | 169,080,000 | 10,895,000 |
| South America | 417,601 | 30,749,000 | 1,776,000 |
| TOTAL | 2,385,365 | 265,977,000 | 39,818,000 |

### COPPER $^{63.57}_{29}$Cu

**316. Occurrence.**—**Copper** (Latin *cuprum,* from earlier *Cyprium, Cyprium aes, i.e.,* Cyprian bronze, from Greek **Cyprus,** anciently renowned for its copper mines) was perhaps the first metal employed by man, by reason of the fact that it occurs in quantity in the free state.

The Indians used the native copper occurring in the Lake Superior region; and commercial production from these deposits commenced in 1845. This region is no longer the chief producer, however, since only 10% of the U. S. copper came from here in 1938, whereas 50% came from Arizona.

Some of the more important copper ores are

| | |
|---|---|
| Native copper | Cu |
| Chalcopyrite (copper pyrites) | $CuFeS_2$ |
| Chalcocite | $Cu_2S$ |
| Malachite | $Cu(OH)_2$, $CuCO_3$ |
| Azurite | $Cu(OH)_2$, $2CuCO_3$ |
| Cuprite | $Cu_2O$ (in all copper deposits) |

Chalcopyrite accounts for half of the copper ore of the world, and chalcocite for another 25 per cent.

Chile and Rhodesia have increased considerably in importance during the past decade since they can produce at a lower cost than the United States. As a result, the basic copper price is lower, and London has replaced New York for foreign copper. However, the British Empire does not exercise a monopoly, since the still larger Chilean deposits are managed by American interests and the U. S. itself produced over ⅓rd the world supply of copper.

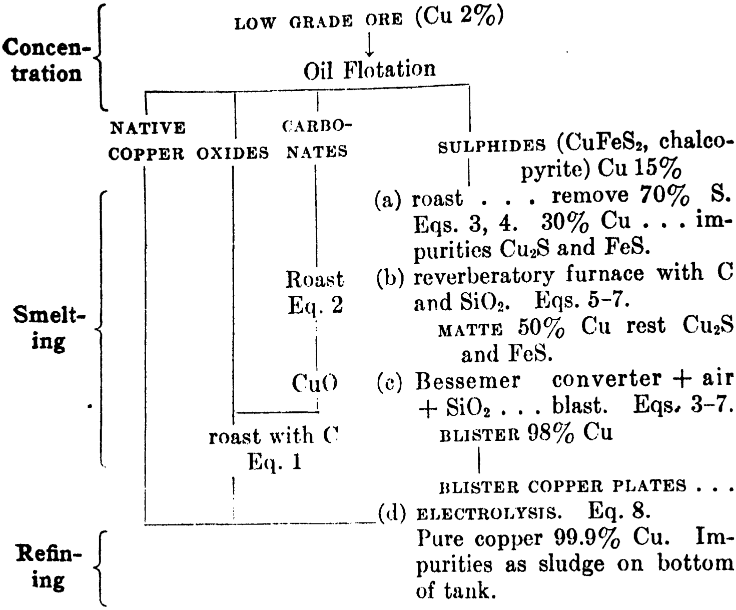
**317. Metallurgy.**—Following the preliminary crushing, grinding and washing processes, the ore may be smelted to remove the gangue, or more often concentrated by the flotation process (290). The subsequent treatment of the ore is outlined in Table 67.

**318. Treating Sulfide Ores.**—Sulfide ores account for three-quarters of all copper metallurgy. The metallurgy involves a number of steps, given in Table 67.

(a) *The ore is roasted to remove about 70 per cent of the sulfur.* Once the roasting is started, no fuel is required. The charge is heated to redness, but not melted.

(b) *The roasted ore is treated to obtain a matte.* The heated material is introduced into enormous furnaces of the reverberatory type, some of which are 100 feet by 30 feet and handle 1500 tons of ore daily. These furnaces are lined with silica brick and have bottoms of magnesite. Coal, oil or gas is blown in. Siliceous ores and limestone may be added as flux. A large part of

TABLE 67. THE METALLURGY OF COPPER



(a) roast . . . remove 70% S. Eqs. 3, 4. 30% Cu . . . impurities $Cu_2S$ and FeS.

(b) reverberatory furnace with C and $SiO_2$. Eqs. 5–7. MATTE 50% Cu rest $Cu_2S$ and FeS.

(c) Bessemer converter + air + $SiO_2$ . . . blast. Eqs. 3–7. BLISTER 98% Cu

BLISTER COPPER PLATES . . .

(d) ELECTROLYSIS. Eq. 8. Pure copper 99.9% Cu. Impurities as sludge on bottom of tank.

The chief reactions which occur are:

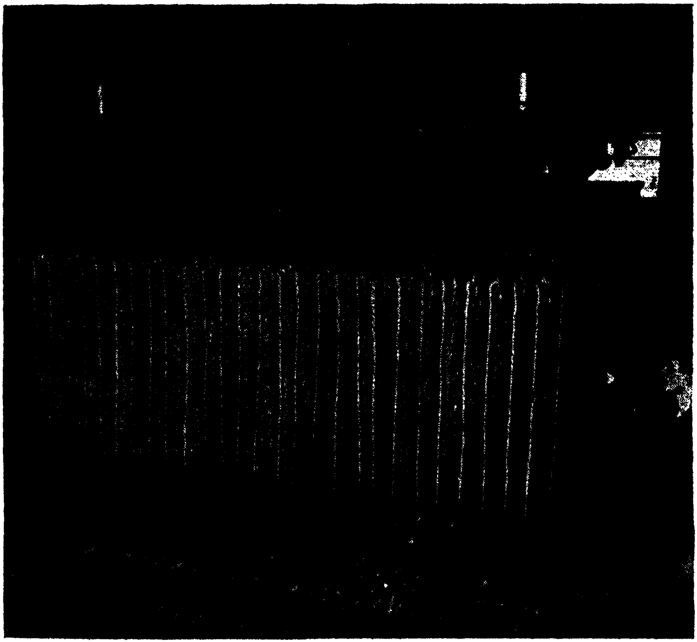
(1) $Cu_2O + C \rightarrow 2Cu + CO$; $CuO + C \rightarrow Cu + CO$
(2) $CuCO_3 \rightarrow CuO + CO_2$
(3) $Cu_2S + O_2 \rightarrow 2Cu + SO_2$
(4) $Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$
(5) $2FeS + 3O_2 \rightarrow 2FeO + 2SO_2 + 221{,}920$ cals.
(6) $Fe_2O_3 + C \rightarrow 2FeO + CO$
(7) $FeO + SiO_2 \rightarrow FeSiO_3$ (slag)
(8) $Cu^{++} + 2e \rightleftarrows Cu^{\circ}$

the iron passes into the slag and a molten mixture of sulfides of copper and iron is obtained, which is known as a **matte.** It contains 40–50 per cent of copper. Gold, silver, and base metals enter the matte.

(c) *In a Bessemer converter* (Fig. 121) *65 tons or more of matte is mixed with siliceous ore (to flux the iron) and air is blasted through the molten mass for several hours.* The sulfur is oxidized to sulfur dioxide, the iron oxide unites with silica to form a slag (equation 7), while the cuprous sulfide and oxide interact to form copper (equation 4). The product is cast into **blister pigs,** which are further refined, in a separate furnace, and cast into **anode plates.**

*Courtesy of the Anaconda Copper Mining Company*

FIG. 121. Pouring molten copper from a Bessemer converter.



*Courtesy of the Anaconda Copper Mining Company*

FIG. 122. Lifting copper cathodes out of the electrolytic tank.

(d) The large anode plates are lowered into an electrolytic bath, and pure copper is deposited on the cathode. Blister copper anodes, each weighing several hundred pounds, are arranged in the bath alternating with thin starting sheets of pure copper which serve as cathodes. (Fig. 122.) The electrolyte is a solution of cupric sulfate and sulfuric acid. A properly regulated current is passed through, and copper is carried from the anode to the cathode where it is deposited. Certain impurities (iron, zinc, lead and nickel) dissolve, while others, such as silver and gold, collect on the bottom of the tank as a mud (slime) which is worked over for the precious metals. Selenium, tellurium, and other valuable by-products are obtained in the refining of copper. A representative electrolytic copper cathode contains 99.98 per cent of the metal.

(e) Finally the cathode copper is melted and cast into commercial shapes and sheets, or these may be rolled into bars, drawn into wires, and so forth.

**319. Properties.**—Copper is red by reflected light and greenish by transmitted light. It is very malleable and ductile, and is the most commonly used conductor of electricity, to which use one-third of all copper finds its way. Copper is reacted upon by dilute and concentrated nitric acid, and by hot concentrated sulfuric acid; but in neither case is hydrogen evolved, since copper is below hydrogen in the electromotive series of metals.

**320. Copper Alloys.**—Copper is used very extensively in the manufacture of wire (conductors, etc.), vessels of various types, stills, roofs, bottoms of ships, and alloys: *e.g.*, brass and bronze. **Brass** is essentially an alloy of copper and zinc, containing from 18–40 per cent of the latter; it is harder and stronger than either copper or zinc, and works much better in a lathe. It is used in the manufacture of sheets, tubes, cartridges, etc. **Bronze** is ordinarily copper alloyed with tin, as well as with zinc and lead (Cu 88 per cent, Sn 8, Zn 2, Pb 2). The percentage of the metals in bronze may vary considerably. The alloy makes strong valves and fittings. An ordinary **penny** is not pure copper, but contains 1 per cent zinc, and 4 per cent tin as well. **Aluminum bronze** commonly contains 90 per cent of copper and 10 per cent of aluminum; it is hard, non-corrosive, and ornamental. **Silicon bronze** contains not more than 4 per cent of silicon, and a small amount of manganese. This resists corrosion better than copper and, because of this property, is used extensively by the chemical industry. **Phosphor bronze** contains tin and phosphorus, in addition to copper, and finds employment in certain parts of machinery. **Manganese bronze** is a brass containing 3% of Mn; propellers of ships are made of it. **Bell-metal** (bells, gongs) contains 75–80 per cent of copper and 25–20 of tin. **Gun-metal** contains 88 per cent of copper, 10 of tin and 2 of zinc.

**321. Electrotype.**—The copper electrotype from which this text is printed is made by preparing a plaster of Paris, wax, or gutta percha cast of the type, after which it is coated with graphite to render it a conductor, and is then employed as a cathode in an electrolytic cell, which contains a solution of cupric sulfate. When the deposit of copper is stripped off, it shows an exact reproduction of the type, engraving, etc. The electrotype, before use in printing, is strengthened and thickened by filling the back with melted lead.

**322. Copper Compounds.**—Copper forms two classes of compounds, cuprous ($Cu^+$) and cupric ($Cu^{++}$). Cuprous compounds are more stable at higher temperatures, less stable in the presence of moisture. Cuprous compounds are less soluble in water, form colorless solutions, and are active reducing agents. Cupric compounds form blue solutions ($Cu(H_2O)_4^{++}$) and often oxidize organic compounds.

**Cupric sulfate, $CuSO_4$,** is the most important salt of copper, being used on a large industrial scale. It is obtained in the refining of silver and by the oxidation of sulfides containing copper:

$$CuS + 2O_2 \rightarrow CuSO_4.$$

The salt also is prepared by dissolving granulated copper in dilute sulfuric acid in the presence of air:

$$2Cu + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O.$$

Cupric sulfate, under ordinary conditions, crystallizes with five molecules of water, forming **blue vitriol** or **bluestone,** $CuSO_4, 5H_2O$. When heated it loses its water of hydration, forming the anhydrous salt $CuSO_4$, which is white.

Cupric sulfate is used in electroplating, the refining of copper, calico printing, as a germicide, insecticide and fungicide, and in preparing other copper compounds. Copper sulfate is sometimes employed to kill algae in water supplies; also, seeds of cereals, before planting, may be treated with a dilute solution of the salt to prevent the growth of fungi, known as smuts.

**323. Complex Ions.**—When a solution of a cupric salt is treated with a small amount of ammonium hydroxide, pale blue cupric hydroxide precipitates:

$$CuSO_4 + 2NH_4OH \rightarrow Cu(OH)_2 \downarrow + (NH_4)_2SO_4.$$

DEMONSTRATION 101. FORMATION OF AMMINE COMPLEXES

Materials: Three test glasses, ammonium hydroxide; solutions of copper sulfate, silver nitrate, sodium chloride, mercurous nitrate and nitric acid.

If the cupric salt is treated with an *excess* of ammonium hydroxide, however, the cupric hydroxide redissolves to form a complex ammonia compound, $Cu(NH_3)_4SO_4$:

$$CuSO_4 + 4NH_4OH \rightarrow Cu(NH_3)_4SO_4 + 4H_2O.$$

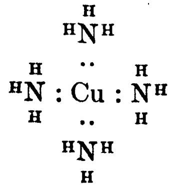
The compound $Cu(NH_3)_4SO_4$ is called copper-ammonia-sulfate or, more formally, tetra-ammine cupric sulfate. E. Werner devoted his life to a study of compounds of this type, in particular the complex cobalt ammines (442). Silver likewise forms complex ammines; one employed in separating AgCl from $Hg_2Cl_2$ in qualitative analysis is $Ag(NH_3)_2Cl$. This may be demonstrated by adding silver nitrate to sodium chloride, followed by an excess of ammonium hydroxide. The silver chloride which at first precipitates, redissolves in the ammonium hydroxide. With a mixture of silver chloride and mercurous chloride, $NH_4OH$ dissolves the silver (as $Ag(NH_3)_2^{++}$) and turns the mercury salt black ($HgNH_2Cl + Hg$).

**Complex cyanides** are also formed by members of Group I-B, in marked contrast to the alkali metals (I-A) which form no complex ions. The complexes $Na^+[Au(CN)_2]^-$ and $Na^+[Ag(CN)_2]^-$ are examples of this, and are used in the cyanide process and in electroplating. The copper complex $[Cu(CN)_2]^-$ is so slightly dissociated into $Cu^+$ and $CN^-$ that it will not precipitate copper sulfide when $H_2S$ is added. This fact is utilized in separating $Cd^{++}$ from $Cu^{++}$ in qualitative analysis, inasmuch as the cadmium cyanide complex ionizes sufficiently:

$$[Cd(CN)_4]^= \rightleftarrows Cd^{++} + 4CN^-,$$

to precipitate cadmium sulfide, leaving the cuprous cyanide ion $[Cu(CN)_2]^-$ in solution.

In the foregoing complexes, copper exhibits a **residual valence,** by sharing electrons with the CN, $NH_3$ or other groups:



$$\begin{array}{ccccc} & & \mathrm{H} & & \\ & & \mathrm{H\,N\,H} & & \\ \mathrm{H} & & \cdot\cdot & & \mathrm{H} \\ {}^{\mathrm{H}}\mathrm{N} & : & \mathrm{Cu} & : & \mathrm{N}^{\mathrm{H}} \\ \mathrm{H} & & \cdot\cdot & & \mathrm{H} \\ & & \mathrm{H\,N\,H} & & \\ & & \mathrm{H} & & \end{array}$$

Tetrammine cupric ion

$$NC : Au : CN$$

Gold cyanide ion

Metals with a large number of electrons in the completed subshell often exhibit this residual valence. The valence bond is called **coordinate covalence,** and the number of groups the metal takes up is known as its **coordination number.** Thus copper has a coordination number of 4; silver, 2; and cobalt, 6 (*e.g.*, $Co(NH_3)_6Cl_3$; or $(Co(NH_3)_5OH)Cl_2$.

### SILVER. ${}^{107.88}_{47}Ag$

**324. Occurrence.**—Silver occurs native, usually scattered throughout a rocky matrix. By far the most important ore of silver though is **argentite,** $Ag_2S$, which is associated with copper and lead sulfides.

In 1939 approximately half of the silver produced in the United States came from sulfide minerals too low in other metals (Cu, Pb, Zn) to make it profitable to extract anything but the silver; another quarter came from copper sulfide ores; and the remainder came from mixed ores of lead-zinc, zinc-copper and zinc-lead-copper.

Of 169,080,000 fine ounces of silver produced in North America in 1939, Mexico supplied 75,870,575 ounces, the United States, 63,871,972 ounces, and Canada, 23,116,861 ounces.

**325. Metallurgy.**—92.2% of the silver produced in the United States in 1939 came from smelting furnaces. Lead ore is added to the silver ore, and the mixture smelted to form an alloy of lead and silver. The alloy is then treated by the **Parke's Process.** In this process, the alloy is melted in large kettles, and 1% zinc is added. The zinc does not dissolve in the lead, but rises to the top, carrying with it any silver, gold and copper (*e.g.*, these metals are considerably more soluble in zinc than in lead; see law of partition, 158). Upon cooling the molten metals, the zinc bearing the silver, gold and copper forms a crust which may be skimmed off. The scum is finally heated in a retort; the zinc volatilizes off and may be returned to the first step of the Parke's process.

Gold contained in silver obtained by the Parke's process is recovered by an electrolytic method. Plates of the silver-gold alloy constitute the anodes, a solution of silver nitrate being employed as electrolyte. Silver is more active than gold, so it forms ions which are discharged at the cathode. The less active gold is collected in a bag surrounding the anode.

In the United States in 1939 7.1% of the silver came from the **cyanidation process.** Air is bubbled through an aqueous solution of sodium cyanide and the ore:

$$O_2 + 2H_2O + 4Ag + 8NaCN \rightarrow 4NaOH + 4NaAg(CN)_2,$$

and

$$Ag_2S + 4NaCN \rightarrow 2NaAg(CN)_2 + Na_2S.$$

The silver may be precipitated by zinc dust or aluminum powder, or by electrolysis.

In 1939 in the United States 0.4% of the silver came from the **amalgamation process**, which is applicable both to native ores and to the relatively unimportant silver chloride ore, *ceragyrite* or horn silver. The crushed ore is treated with mercury and the amalgam then heated in an iron retort, the volatile mercury being expelled. Mercury first displaces silver from silver chloride, and then forms an amalgam with it:

$$2AgCl + 2Hg \rightarrow 2Ag + Hg_2Cl_2.$$

**326. Properties.**—Pure silver is a white, lustrous crystalline metal, very malleable and ductile, and capable of taking a high polish. Silver sheet 1/10,000 of an inch thick has been prepared. Molten silver absorbs about 22 times its volume of oxygen, which escapes as the metal solidifies, giving rise to the phenomenon of "spitting." Silver conducts heat and electricity better than does copper.

Silver does not combine directly with oxygen, even at high temperatures. On the other hand it combines with sulfur to form silver sulfide. Thus, when the metal is exposed to hydrogen sulfide it tarnishes quickly on account of the formation of a film of silver sulfide. **"Oxidized silver"** is made by treating silver objects with a solution of potassium hydrogen sulfide (KHS), a thin film of the sulfide being formed. Silver reacts readily with nitric acid, forming silver nitrate; and with hot concentrated sulfuric acid, forming silver sulfate.

**327. Silver Compounds.**—When a soluble silver salt is treated with sodium hydroxide, brown **silver oxide, $Ag_2O$,** is obtained. Silver hydroxide is no doubt formed, but it decomposes

$$\begin{array}{l} 2AgNO_3 + 2NaOH \rightarrow 2NaNO_3 + \quad 2AgOH \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad Ag_2O + H_2O. \end{array}$$

An aqueous solution of silver oxide is distinctly alkaline, so that silver hydroxide is regarded as moderately active. As with HgO (32), the decomposition of $Ag_2O$ is a reversible reaction.

**Silver nitrate,** or lunar caustic, $AgNO_3$, is a salt of great value. It is prepared by dissolving silver in dilute nitric acid:

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + 2H_2O.$$

It crystallizes in large rhombic plates which melt at 208.6°. The salt is very soluble in water.

Silver nitrate is a powerful oxidizing agent, and is often cast in the form of sticks for use in surgery. When silver nitrate is brought in contact with the skin, cloth, or other organic matter, a black stain is produced, because of the reduction of the salt to metallic silver. The salt therefore finds application in the manufacture of "marking inks" and hair dyes. (See 330.)

Silver salts practically insoluble in water are the white *chloride* ($AgCl$); yellow *bromide* ($AgBr$), *iodide* ($AgI$), and *phosphate* ($Ag_3PO_4$); red *chromate* ($Ag_2CrO_4$); brown *arsenate* ($Ag_3AsO_4$), and black *sulfide* ($Ag_2S$). On the other hand *silver fluoride* is very soluble in water.

**328. Photography.**—Insoluble silver chloride, bromide and iodide react with a number of salts forming soluble complexes. **Sodium thiosulfate,** photographers **hypo,** is one of these:

$$\underset{\text{insoluble}}{AgBr} + 2Na_2S_2O_3 \rightarrow \underset{\text{soluble}}{Na_3Ag(S_2O_3)_2} + NaBr.$$

In photography, cellulose acetate (safety film), cellulose nitrate, or glass plates are coated with a gelatin in which a mixture of silver bromide and iodide is suspended.

### DEMONSTRATION 102. PRINCIPLE OF PHOTOGRAPHY

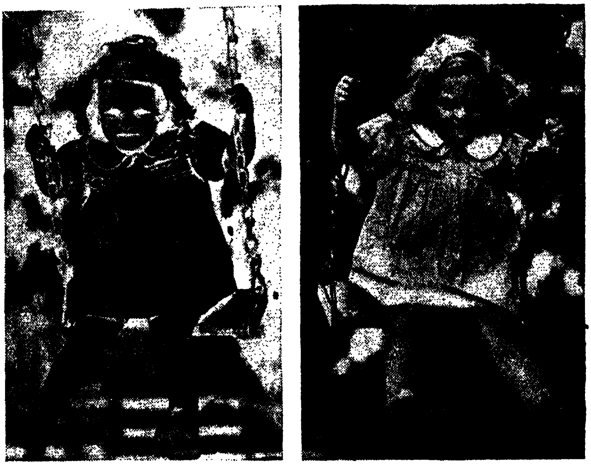
Materials: Two test-glasses, silver coin, solutions of silver nitrate, sodium thiosulfate, potassium bromide and iodide; magnesium ribbon, tongs, burner, photographic film, a negative, a positive, photographic developer.

Demonstrate the principles of photography as described below. When sodium thiosulfate solution is added to a test glass containing a silver coin and a precipitate of silver iodide, the coin is unattacked, while the precipitate dissolves. See Demonstration 72, section 201.

If a photographic film is exposed to light, invisible **grains of silver** are formed. If this is then treated with certain reducing agents, called **developers** (an alkaline solution of a weak reducing agent such as hydroquinone, pyrogallol, ferrous oxalate, or, for fine-grain, para-phenylene-diamine) the silver salts immediately surrounding the grains of silver are acted upon more readily. The grains therefore grow in size until they become visible; *i.e.*, they are developed into a black film of silver, or **negative.** After this, the film is treated with a **fixer** (hypo, sodium thiosulfate) which dissolves away the portions of unreduced silver salts, leaving the silver negative intact (Fig. 123).

The development and fixing of the positive print is similar to that of the negative. Prints may be toned by treating them with gold or platinum compounds; these metals displace the silver and add beauty to the final photograph.

**Orthochromatic** emulsions contain certain dyes which render the silver salts sensitive to the blue-green end of the spectrum. Since the red end of the spectrum does not decompose this film, the photographer may work under a safety red-lamp. By adding other organic dyes to the photographic emulsions, they can be made sensitive to red, and even to infra-red light. Such films are called **panchromatic,** since they are affected by *all* colors of the visible spectrum. A rainbow photographed with panchromatic film would faithfully reveal the red as well as the blue portions. Photosensitizing dyes which are sensitive to infra-red light enable the aviator to photograph through the haze which appears to surround a distant mountain. An audience has been photographed in the dark using infra-red flood-lights.



*Courtesy of the Eastman Kodak Company*

FIG. 123. Photographic negative and positive.

**329. Complex Silver Ions.**—The formation of the ion $Ag(S_2O_3)_2^{=}$ in photography has been mentioned (326). Also, the complex ion $Ag(NH_3)_2^+$ was demonstrated (Demonstration 101) when silver chloride was dissolved by adding ammonium hydroxide to form diammine silver chloride, $Ag(NH_3)_2Cl$.

When a solution of a silver salt or a halide of silver is treated with potassium cyanide, insoluble silver cyanide (AgCN) is first formed, which dissolves in excess of the reagent, forming **potas-**

**sium silver cyanide,** $KAg(CN)_2$:

$$AgBr + KCN \rightarrow AgCN + KBr,$$
$$AgCN + KCN \rightarrow KAg(CN)_2.$$

This silver salt is employed in **electroplating.** The article to be plated is the cathode, a plate of silver is the anode, and a bath of potassium silver cyanide serves as electrolyte. The complex silver salt ionizes thus:

$$KAg(CN)_2 \rightleftarrows K^+ + Ag(CN)_2^-$$
$$\downarrow\uparrow$$
$$Ag^+ + 2CN^-.$$

A very low concentration of the silver ion is present, but when it is discharged, more of the complex ion is formed. The following change occurs at the cathode:

$$Ag^+ + \ominus \rightarrow Ag.$$

The potassium ion is not discharged, for potassium requires a much higher E.M.F. for its liberation than does silver.

**330. Uses for Silver.**—We have already discussed silver in photography (328), and silver plating (329).

### DEMONSTRATION 103. SILVER MIRRORS

Materials: *Solution* (*a*): add $NH_4OH$ to 10 g. $AgNO_3$ in water until the precipitate which first appears, redissolves. Filter and dilute to 1 liter. *Solution* (*b*): 2 g. $AgNO_3$, 1.66 g. Rochelle salt ($KNaC_4H_4O_6$) in 1 liter of distilled water.

**Silver mirrors** may be produced by mixing equal volumes of solutions (a) and (b), warming if necessary. The silver ion is reduced by tartrates, glucose or aldehydes. In 1940 this same reaction was improved as an industrial process so that the two solutions are now sprayed on, instantly silvering the glass against which they are sprayed.

Silver lined kettles are used in jam and fruit factories, and in other food industries because acids do not corrode them.

Silver is so soft that it is usually **alloyed with copper** to increase its hardness. Our silver coinage has a "fineness of 900" which means 900 parts of silver and 100 parts of copper. Sterling silver has a fineness of 925.

In the 12th century the Hanseatic League proffered silver coins in exchange for British cattle and grain. The British referred to these German tradesmen as "Easterlings," and the name was later changed to sterling.

**Sheffield plate** was originally made by bonding a sheet of silver to copper; but today imitation Sheffield is made by electrodepositing silver on copper. **German silver** (nickel silver) contains nickel, copper and zinc, but no silver.

### GOLD $^{197.2}_{79}Au$

**331. Occurrence.**—Gold occurs largely in the native condition, hence it was one of the first metals used by man.

The metal is mentioned in ancient writings, the earliest words for the metal in Hebrew and in Egyptian referring to its shining appearance. The ancients considered it to be the noblest of metals. Flint daggers with gilt handles have been found in Egyptian excavations, and gold was coined hundreds of years B.C.

Free gold is not abundant, but is widely distributed. The metal is disseminated in veins of quartz, and is usually associated with other metals, such as silver, copper or iron; it also occurs mixed with alluvial sand and gravel. Many minerals, such as iron pyrites, galena, and zinc blende, contain very small quantities of gold.

Amalgamation methods for extracting gold from seawater were investigated by Fritz Haber (514) in 1919; and the Dow Chemical Company in 1940 actually exhibited tiny gold buttons made this way at their bromine-from-seawater plant in North Carolina (602). Concentration of gold in seawater varies from 14 parts per million in shallow waters to 0.02 parts in the deep seas.

Most of the United States gold comes from California and Alaska, South Dakota and the western states. These states and the Union of South Africa account for more than half of world production (315).

**332. Metallurgy.**—Gold is produced by much the same processes as silver. In the United States in 1939 the amalgamation process produced 21.1% of our gold, the cyanidation process 22.3%, smelting 28.0%, and placer mining 28.6%.

**Placer mining** consists in washing alluvial deposits in a sluice box. This is merely an elaboration of the crude cradling or panning method of the prospector. On account of its high density gold settles to the bottom and the lighter material is washed away. In "hydraulic mining" a powerful stream of water is employed to wash the gold and earthy matter into the sluices.

The **amalgamation process** may be employed to catch the particles of gold which escape through the sluices. The dirt and gold leaving the sluices are washed over amalgamated copper plates or cleats. By heating the gold amalgam, mercury is volatilized.

The **cyanide process** for gold is similar to that for silver:

$$4Au + 8NaCN + 2H_2O + O_2 \rightarrow 4NaAu(CN)_2 + 4NaOH.$$

The gold may be precipitated by means of zinc or aluminum, or electrolytically. The method is applicable to very low-grade ores and "tailings," and it has increased the production of gold enormously since its introduction in 1890, particularly in South Africa.

Gold may be purified by electrolysis or by cupellation. It may be separated from silver and many other metals by heating the alloy with strong sulfuric acid, the gold being insoluble.

**333. Properties.**—Gold, in the massive state, is a yellow, shining metal; but if it be precipitated in a finely divided condition, *e.g.*, by the addition of ferrous sulfate to a solution of the chloride, the metal has a brownish color by reflected light. Gold leaf by transmitted light possesses a green or blue color. Its melting point is 1,063° and the density is 19.3. Gold is the most malleable and ductile of metals. The metal can be deposited in extremely thin layers: *e.g.*, the deposit on gold lace is about 0.000002 mm. thick!

The metal is soft, so it must be alloyed with copper and other metals to increase its hardness. Green gold contains silver, zinc or cadmium; blue gold contains iron; purple gold is an alloy of aluminum; and nickel gives white gold.

Only a few chemical reagents attack gold. It is attacked, however, by fused alkalies and nitrates and by phosphorus; and dissolves in *aqua regia* to form chlorauric acid, $HAuCl_4$ (or $HCl, AuCl_3$); it is dissolved by liquids containing free chlorine or bromine, and by solutions of the alkali cyanides in the presence of air. Gold is much more resistant than are copper and silver.

Gold may be detected by warming a solution of stannic and stannous chlorides with a very dilute gold salt, whereupon the gold is reduced to the colloidal state, *purple of Cassius.*

Gold, like copper and silver, can be precipitated as the sulfide; these sulfides are soluble in alkali sulfides.

**334. Gold Compounds.**—Gold forms $Au^+$ (aurous) and $Au^{+++}$ (auric) compounds (*e.g.*, $Au_2O$ and $Au_2O_3$; $Au_2S$ and $Au_2S_3$; $AuCl$ and $AuCl_3$. **Auric chloride** is a water-soluble, red crystalline solid. It decomposes on heating:

$$\begin{array}{l} 2AuCl_3 \rightarrow 2Cl_2 + 2AuCl \\ \qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\quad\;\; 2Au + Cl_2. \end{array}$$

**Chlorauric acid,** $HAuCl_4$ is formed by dissolving gold in aqua regia.

### 335. Compounds in Group I-B.—

TABLE 68. GROUP I-B: USES

| | |
|---|---|
| **Copper and its compounds** | **Cu (319); alloys (320); $CuSO_4$ (322); complex ions (323).** |
| Bordeau mixture<br>$CuSO_4$ + milk of lime | spraying vegetation, insecticide. |
| Cupric acetate (basic)<br>verdigris<br>green: $CuO, 2Cu(C_2H_3O_2)_2$<br>blue: $CuO, Cu(C_2H_3O_2)_2$ | pigment, textile printing; wood preservative. |
| Cupric aceto-arsenite<br>Paris green<br>$Cu(C_2H_3O_2)_2, Cu_3(AsO_3)_2$ | poisonous; fungicide, preserving wood; insecticide (*e.g.*, potato beetle). |
| Cupric carbonate (basic)<br>$Cu(OH)_2, CuCO_3$ | 319; ancient patina; insecticide; in pyrotechnics. |
| Cupric chloride<br>$CuCl_2, 2H_2O$ | mordant; catalyst; wood preservative; water purification; photography. |
| Cuprous chloride<br>$Cu_2Cl_2$ | absorbent for $CO$, $O_2$, $C_2H_2$, and other gases. |
| Cuprous cyanide<br>$Cu_2(CN)_2$ | very poisonous; electroplating. |
| Cupric nitrates<br>$Cu(NO_3)_2, 6H_2O$<br>$Cu(NO_3)_2, 3H_2O$ | insecticides; electroplating; coloring metals; mordant; photography. |
| Cupric organic salts (oleate, resinate, stearate) | copper with an organic acid; for anti-fouling paints. |
| Cupric oxide | removing Sulfur compounds from petroleum. |
| Cuprous oxide;<br>ruby copper; $Cu_2O$ | colors glass ruby-red; ceramics; mild reducing agent. |
| **Silver and its compounds** | **Ag (326), $Ag_2O$ (327); $AgNO_3$ (327); other salts (327); AgCl, AgBr and AgI (328); complex salts (329); alloys (330).** |
| Silver nucleinate or nargol | from nucleic acid and a silver salt; an antiseptic. |
| **Gold and its compounds** | **Au (333); $AuCl_3$ (334); $HAuCl_4$ (334).** |
| Auric chloride<br>$AuCl_3, HCl, 3H_2O$ | very soluble in water and alcohol; medicine; toning in photography. |
| Potassium gold cyanides<br>$KAu(CN)_2$ (aurous)<br>$KAu(CN)_4$ (auric) | electrolytes in electro-gilding. |
| Sodium auric chloride<br>$NaAuCl_4, 2H_2O$ | toning reagent in photography. |

## QUESTION REVIEW

I. GENERAL.

**a. Copper, silver and gold; Group I-B (314).**

1. Contrast group I-B with group I-A.

**b. Production statistics (315).**

2. Who are the two chief producers of copper? of silver? of gold?

II. COPPER.

**a. Occurrence (316).**

3. Give the names and formulas of the two chief ores of copper. What change has come about in the copper market during the past decade?

**b. Metallurgy (317). Treating sulfide ore (318).**

4. Outline the metallurgical steps for (*a*) Cu, (*b*) CuO, (*c*) $CuCO_3$, (*d*) chalcopyrite.

**c. Properties (319).**

5. State three physical properties of copper. How does copper react with (*a*) air, (*b*) dilute nitric acid, (*c*) concentrated sulfuric acid?

**d. Copper alloys (320). Electrotype (321). Copper compounds (322).**

6. Why was there no bronze age among the Indians of North America?
7. Contrast the properties of cuprous and cupric compounds.
8. Outline the chemistry of blue vitriol. What is formed when it is treated with $NH_4OH$?

**e. Complex ions (323).**

9. Show that the separation of $Cd^{++}$ from $Cu^{++}$ depends upon the properties of complex ions.
10. Diagram the ion $Cu(NH_3)_4^{++}$, showing how copper exercises its residual valence. What is the name given to this type of valence bond?

III. SILVER.

**a. Occurrence (324). Metallurgy (325). Properties (326).**

11. Describe (*a*) the Parke's process, (*b*) amalgamation, (*c*) cyanidation. What % of U. S. silver is recovered by each of these processes?

**b. Silver compounds** (327).

12. Contrast silver hydroxide with potassium hydroxide. What silver salts are soluble?

**c. Photography** (328).

13. Explain each of the following: fixer, developer, silver grain, a photographic negative, complex salt in photography, toning, photosensitizing, infra-red photography.

**d. Complex silver ions** (329).

14. What properties of complex silver ions make them useful in (*a*) separating $Hg_2Cl_2$ from AgCl, (*b*) silver electroplating?

**e. Uses for silver** (330).

15. What is meant by sterling silver? Sheffield silver? German silver? How are mirrors silvered? What per cent silver is in a dime?

IV. GOLD.

**a. Occurrence** (331). **Metallurgy** (332). **Properties** (333).

16. What part does each of the following play in the metallurgy of gold: (*a*) water, (*b*) mercury, (*c*) sodium cyanide?

**b. Gold compounds** (334).

17. What is green gold? Purple of Cassius? White gold? 18 carat gold?
18. Give the chemistry of gold chlorides.

V. INDUSTRIAL USES OF GROUP I-B (335).

19. Give the name, formula, and one important use of 10 group I-B compounds.

**Reading References:** Articles in the Appendix:

*Copper:* 21, 27, 52, 131, 229, 236 and 404.

*General:* 49, 61, 64 and 228.

*Silver:* 9, 111, 127 and 219.

*Gold:* 109, 118 and 219.

# CHAPTER XXVI

# THE ALKALINE EARTH METALS. GROUP II-A

**336. Characteristics of Group II-A.**—The alkaline earth family includes beryllium, magnesium, calcium, strontium, barium, and radium. Originally their oxides were called the "alkaline earths" because they resembled not only the alkalies, but also the earths (*e.g.*, the oxides of iron and aluminum were "earths"). Although radium belongs in the family, it has been considered elsewhere because of its unique property of nuclear disintegration (246).

TABLE 69. GROUP II-A. THE ALKALINE EARTH METALS

| Element | Atomic Weight | Atomic Number | Electronic Structure | Density | Melting Point |
|---|---|---|---|---|---|
| Beryllium, Be | 9.02 | 4 | 2–2 | 1.85 | 1350° |
| Magnesium, Mg | 24.32 | 12 | 2–8–2 | 1.74 | 651° |
| Calcium, Ca | 40.08 | 20 | 2–8–8–2 | 1.55 | 810° |
| Strontium, Sr | 87.63 | 38 | 2–8–18–8–2 | 2.6 | 752° |
| Barium, Ba | 137.36 | 56 | 2–8–18–18–8–2 | 3.5 | 850° |
| Radium, Ra | 226.05 | 88 | 2–8–18–32–18–8–2 | 5 | 960° |

As regards **physical properties,** all of the alkaline earth metals are silvery, soft, and malleable, though less so than the alkali metals. Their hardness decreases with increasing atomic weight, barium being about as soft as lead. They are good conductors of electricity, although somewhat brittle.

**Chemical reactions of the elements,** particularly of the last four members of the series, are extremely alike. On the other hand magnesium, and especially beryllium, show many anomalies because of the smallness of their ions; this binds them tightly to other ions. They are all bivalent, as would be anticipated from the fact that each possesses two outermost electrons in the *s* level. With the exception of beryllium, these electrons are rather easily removed; the alkaline earth metals are only a little less active than the alkali metals, the activity increasing with increasing atomic weight. Beryllium and magnesium do not form hydrides; but calcium, strontium, barium and radium do so readily at 600°. Heated in air, they unite with oxygen and with nitrogen to form oxides and nitrides of the type $MO$ and $M_3N_2$. Though beryllium does not react with steam, magnesium does so readily; and the remaining members of the family interact even with cold water to liberate hydrogen:

$$M + 2HOH \rightarrow M(OH)_2 + H_2.$$

Turning to the **physical properties of compounds** of the alkaline earth metals, we find beryllium to be unique. Unlike most metallic halides (*e.g.*, fluorides, chlorides, bromides and iodides) fused beryllium halides are poor conductors of electricity. Also, they hydrolyze. Fluorides of the alkaline earth family are all insoluble in water, with the exception of beryllium fluoride. The sulfates are also quite insoluble, with the exception of $BeSO_4$.

Be and Mg compounds do not volatilize sufficiently to apply **flame tests,** but the other members of group II-A give characteristic colors: calcium brick-red, strontium crimson, and barium green.

Finally, the **chemical properties of compounds** of the alkaline earths exhibit both similarities to, and striking differences from, those of Group I-A. The oxides dissolve in water to form active hydroxides, the solubility and basic strengths of the hydroxides increasing with increasing atomic weight. Beryllium hydroxide, $Be(OH)_2$, is so feeble that it acts also like an acid ($H_2BeO_2$). We say that it is **amphoteric.** In contrast to the behavior of the corresponding sodium and potassium compounds, the hydroxides and carbonates of the alkaline earth metals are decomposed by heat; and the nitrates also are more easily decomposed than the alkali metal nitrates. $BeCO_3$ does not exist.

**General preparation:** the alkaline earth metals are generally prepared by electrolysis of the fused chloride, fluoride, or hydroxide. They can also be isolated by reducing their halides with sodium or potassium. Magnesium and calcium are the only members prepared in tonnage lots.

## BERYLLIUM $^{9.0}_{4}Be$

**337. Beryllium, Be.**—Beryllium was first prepared by Wöhler in 1828, although Vauquelin had detected its oxide in beryl as early as 1797. Beryllium is sometimes called **glucinum** (Greek, meaning *sweet*), because its salts possess a sweetish taste. Beryllium ores are fairly abundant both in this country and abroad, especially **beryl,** a metasilicate of beryllium and aluminum, $Be_3Al_2(SiO_3)_6$, or $3BeO, Al_2O_3, 6SiO_2$. The mineral beryl usually has a green color, probably due to traces of chromium silicate, but beryl of different colors exists. Beautiful specimens of **emerald,** or transparent green beryl, come from Colombia. At present beryllium ores are a waste product from New England feldspar mines.

Beryllium is prepared by the electrolysis of beryllium oxyfluoride or of the double fluoride $BeF_2, 2KF$ at 400°. Its melting point is 1,350°, density 1.85. When heated in air it forms BeO. Its hydroxide is amphoteric. Some other chemical properties of its compounds are given in the foregoing section.

Beryllium is about 30% lighter than aluminum, but much harder. According to H. S. Cooper, it is over four times as elastic as aluminum, and 25% more elastic than steel. Unlike aluminum, it does not corrode readily when in contact with salt water. Beryllium forms some interesting alloys.

An alloy containing 70% of beryllium and 30% of aluminum is one-third lighter than is aluminum, far more resistant to corrosion, with tensile strength far greater than that of duralumin. Alloys with nickel are resistant to salt-water corrosion. Beryllium is to copper what carbon is to iron, for a trace enormously increases its strength (432). Thus addition of 2% beryllium to copper produces an alloy which, on further working, is five times more resistant to wear than phosphor bronze. This beryllium bronze is an excellent material for springs, particularly where there is danger of corrosion or magnetization. In 1939 beryllium metal was placed in commercial production in the United States.

## MAGNESIUM $^{24.3}_{12}Mg$

**338. History and Occurrence.**—This element derives its name from *Magnesia*, a town in Asia Minor. Davy isolated the metal in the impure state, in 1808. Bussy, in 1829, first obtained it as a coherent metal by fusing its chloride with potassium. Bunsen subsequently prepared magnesium by the electrolysis of its chloride.

Magnesium occurs in combination in great abundance and is very widely distributed, constituting 2.1 per cent of the solid shell of the earth. Sea-water is 0.5 per cent magnesium, calculated as magnesium chloride.

Important magnesium minerals are:

| | |
|---|---|
| Magnesite | $MgCO_3$ |
| Dolomite (magnesian limestone) | $MgCO_3$, $CaCO_3$ |
| Talc or soapstone | $H_2Mg_3(SiO_3)_4$ |
| Meerschaum | $H_4Mg_2(SiO_3)_4$ |
| Carnallite | $MgCl_2$, KCl, $6H_2O$ |
| Kieserite | $MgSO_4$, $H_2O$ |
| Asbestos | $CaMg_3(SiO_3)_4$ |

Part of the calcium in limestone is sometimes displaced by magnesium, giving rise to **dolomite,** millions of tons of which are consumed each year in the steel industry. *Talc* abounds along the Atlantic coast; *carnallite* and *kieserite* are plentiful in the Stassfurt salt beds; and over half of the world's *asbestos* comes from Thetford Mines, Canada, just south of the St. Lawrence River.

**339. Metallurgy.**—Magnesium is manufactured by the electrolysis of magnesium oxide dissolved in a bath of molten fluoride, principally magnesium fluoride. The process is somewhat similar to the Hall process for producing aluminum (377). The anodes are carbon, which are oxidized to carbon dioxide by the liberated oxygen. The metal is set free at the cathodes, the oxide being added continuously.

Germany produced 16,500 tons, two-thirds of the world's magnesium, in 1939; the United States lagged far behind (4831 tons) because of the availability and simpler metallurgy of aluminum, for which magnesium is usually substituted. However, the Dow Chemical Company, sole domestic producer, is expected to produce 12,500 tons by 1942. In 1941 they opened a $5,000,000 plant at Freeport, Texas, to recover magnesium from sea-water. It has a capacity equal to that of their plant at Midland, which utilizes the Michigan brines. The price is 27¢ per pound, compared with aluminum at 17¢.

**340. Properties.**—Magnesium is a silvery white metal, with a density of 1.74; it melts at 651° and boils at about 1,100°. Just below its melting point it is ductile. When exposed to the air it is slowly coated with a basic carbonate, which protects the metal beneath.

### DEMONSTRATION 104. REACTIONS OF MAGNESIUM

Materials: (*a*) magnesium ribbon, forceps; (*b*) magnesium powder in a covered nickel crucible over burner; tongs, beaker of water, litmus paper; (*c*) 1-liter Erlenmeyer flask with 100 cc. water over burner, deflagrating spoon; (*d*) hydrochloric acid, splint.

Magnesium is quite active chemically. (a) When heated in air it burns brilliantly, forming magnesium oxide, which contains some nitride. (b) Heated in a covered crucible, or in a nitrogen atmosphere, it forms the nitride; upon cooling and (CARE) lowering the crucible into water, ammonia is given off; and the ammonium hydroxide which forms, colors litmus paper blue. It also combines with chlorine. The metal displaces hydrogen from (c) steam and (d) dilute acids. It is a powerful reducing agent similar to thermit in metallurgy.

(*a*) $2Mg + O_2 \rightarrow 2MgO + 291{,}500$ cals.
(*b*) $3Mg + N_2 \rightarrow Mg_3N_2$; and $Mg_3N_2 + 6HOH \rightarrow 3Mg(OH)_2 + 2NH_3 \uparrow$
(*c*) $Mg + 2HOH \rightarrow Mg(OH)_2 + H_2 \uparrow$
(*d*) $Mg + 2HCl \rightarrow MgCl_2 + H_2 \uparrow$.

It cannot be electrodeposited from solutions of its salts.

**341. Uses.**—Magnesium is a strategic war material, and the increased attention given the element in Germany, Japan, England, and the United States reflects this fact. In non-ferrous metallurgy (*e.g.*, copper, aluminum, etc.) it is used as a scavenger to de-oxidize the molten batch. Because of the brilliant light it emits upon burning, it is employed in star shells, flares, tracer bullets, and in one type of photoflash bulb.

Ninety per cent of all the magnesium produced in 1939 went into structural alloys. These alloys possess lightness as well as strength, and since 1938 have been made resistant to corrosion.

**Electron** contains 95% magnesium, 4.5% zinc and 0.5% copper, and is as strong as some of the common cast bronzes. The increasing number of airplane and automobile parts made of magnesium alloys is made possible by better die-casting techniques which have been perfected during the past several years. Still other alloys can be rolled, forged, and extruded. **Dowmetal** is a magnesium alloy containing 4–10% aluminum and a trace of manganese. It has less than one-fourth the density of steel, two-thirds the weight of aluminum, and is comparable in strength with aluminum alloys.

**342. Magnesium Compounds. Magnesium oxide, or magnesia** ($MgO$), is an exceedingly light, white powder prepared by heating the carbonate (magnesite) or by burning magnesium. Magnesia melts at about 2,500°, so it is employed for lining crucibles and furnaces and in the *manufacture of firebrick.* Calcined magnesia is a poor conductor of heat, and for this reason is used on a large scale for insulating pipes and boilers.

Magnesium oxide slowly interacts with water to form the sparingly soluble hydroxide $Mg(OH)_2$, which has an alkaline reaction. Both oxide and hydroxide readily interact with acids to form salts. They are used as antidotes for poisoning by strong acids. *Milk of magnesia* is a suspension of $Mg(OH)_2$ in water.

By treating the moist hydroxide with magnesium chloride, a *hydrated basic chloride*, $(Mg(OH)_2)_x$, $(MgCl_2)_y$, $(H_2O)_z$, is obtained; it is used as a plaster-finish in building.

**Magnesium chloride, $MgCl_2$,** forms white deliquescent crystals, $MgCl_2, 6H_2O$. When the hydrate is heated, partial hydrolysis occurs, hydrochloric acid being liberated:

$$MgCl_2 + 2HOH \rightleftarrows Mg(OH)_2 + 2HCl.$$

When waters containing magnesium salts are used in boilers, the salts are more or less hydrolyzed, forming magnesium hydroxide, which deposits on the boiler tubes. The coating of *boiler scale* means that a larger amount of fuel is required to generate steam. It is difficult to remove the deposit, and now and then the thick scale cracks, which exposes the very hot iron to steam, giving rise to an explosion (why?).

**Silicates containing magnesium,** such as talc, meerschaum, and asbestos, are very important. *Talc* is used in the manufacture of paper and toilet powder; *soapstone or Alberene stone* (a massive rock composed chiefly of talc) is quarried in large blocks and then manufactured into various objects, such as laundry tubs, laboratory tables, hoods, tanks, pots, etc.; *meerschaum* is used for tobacco pipes, cigar holders, etc.; *asbestos* is used as cloth, felt, packing material, and for fireproofing in general.

Other important magnesium compounds are tabulated in section 355.

## CALCIUM $^{40.08}_{20}Ca$

**343. Occurrence.**—Calcium constitutes about 3.6 per cent of the earth's crust, being a constituent of many important minerals and rocks.

By the weathering and decomposition of rocks calcium finds its way into natural waters, to which it imparts "hardness." Calcium occurs very abundantly as the carbonate, $CaCO_3$. Limestone, marble, calcite, chalk, and seashells are familiar forms of calcium carbonate. When waters containing magnesium salts percolate through calcium carbonate, calcium may be partly displaced by magnesium, forming dolomite, $CaCO_3, MgCO_3$. Calcium also occurs abundantly as hydrated calcium sulphate, or gypsum, $CaSO_4, 2H_2O$, and as anhydrite, $CaSO_4$. The phosphate $Ca_3(PO_4)_2$ is found in natural deposits and in bones; fluorspar, $CaF_2$, is another important calcium mineral.

**344. Preparation and Properties.**—Calcium (Latin *calx*, lime) was first obtained by Davy, in 1807, by the electrolysis of fused calcium hydroxide. **It is now prepared by electrolyzing the fused chloride to which calcium fluoride may be added to lower the melting point.** The electrolysis is conducted in a graphite crucible which serves as anode, an iron ribbon or rod being employed as cathode. The calcium adheres to the cathode, which is gradually raised, and a rod of the metal is built up in the form of a "cabbage-stalk." 41,718 pounds were produced in 1939 in the United States, chiefly as a deoxidizer of alloys and steels.

Calcium is a silvery white metal, which turns slightly yellowish on exposure to the air, owing to union with nitrogen. When heated in air, it burns to form a mixture of oxide and nitride. Its density is 1.55 and it fuses at 810°; it is malleable and is a little harder than lead.

Calcium is an active metal and strongly electropositive in character, but less so than are the alkali metals. The metal combines directly with hydrogen, oxygen, nitrogen, the halogens, sulfur, and carbon; it readily decomposes cold water:

$$Ca + 2HOH \rightarrow Ca(OH)_2 + H_2 \uparrow .$$

**345. Calcium Carbonate, $CaCO_3$.**—As previously stated, calcium carbonate occurs very abundantly in nature.

The mineral calcite, or Iceland spar, crystallizes in the hexagonal system; and aragonite, in rhombic prisms. **Limestone** is essentially calcium carbonate, but it contains more or less foreign matter, such as magnesium carbonate, clay, silica, and compounds of iron. Pearls, coral, and many kinds of shells and natural chalk are largely calcium carbonate. **Marble** is crystalline limestone. Carrara marble is noted for its purity and whiteness. **Marl** is a mixture of limestone and clay.

Calcium carbonate may be prepared in the laboratory by the interaction of aqueous solutions of calcium chloride and sodium carbonate:

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaCl.$$

The compound is virtually insoluble in pure water, but soluble in water containing carbon dioxide, forming the bicarbonate, $Ca(HCO_3)_2$, which renders water temporarily hard. When heated to a high temperature, it decomposes with the formation of calcium oxide and carbon dioxide. It reacts with acids, giving carbon dioxide.

Calcium carbonate is used in enormous quantities. Limestone is employed as building stone, crushed stone, fluxing stone, in alkali works, agriculture, and in the manufacture of glass. Large quantities of marble are also used.

**346. Calcium Oxide and Hydroxide.**—Calcium oxide, or "quicklime," CaO, is manufactured on a very large scale by heating limestone in kilns (Fig. 124).

Both continuous and intermittent kilns are employed, but the former type is more economical. To produce a lime free from ash, the fires are built at the sides of the kiln, the gases passing up through the kiln, the lime being removed at the bottom. This is known as the "long-flame" process. In the "short-flame" process a mixture of limestone and fuel is heated in the kiln; the product contains ash. Much lime is now produced in rotary kilns very similar to those employed in the manufacture of cement:

$$CaCO_3 \rightarrow CaO + CO_2 - 41{,}830 \text{ cals.}$$

In consideration of Van't Hoff's Laws (216) we should suppose that to drive this reaction to the right, high temperature should be employed. At 900° C. the equilibrium is almost wholly to the right. In practice, however, the carbon dioxide is swept away in a current of air, thus driving the reaction to completion (224, b). By this device the kiln operates at a lower temperature; this avoids the formation of fusible silicates (slag) which would fill the pores of the lime and interfere with the subsequent slaking process.

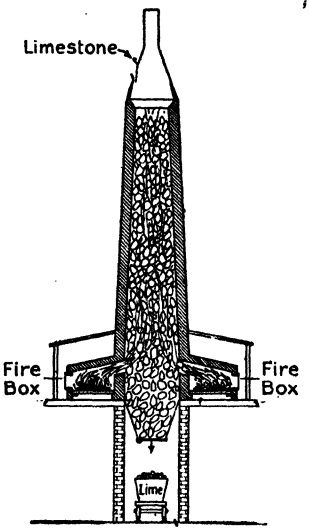


FIG. 124. Lime kiln for the "long flame" process.

DEMONSTRATION 105. PROPERTIES OF LIME

Materials: Fresh quicklime in beaker, oxyhydrogen flame directed towards lump of quicklime, litmus paper, 10-inch length of 6 mm. glass tubing.

**Lime,** $CaO$, gives a blinding glow (limelight) in the oxyhydrogen flame; but it does not melt until 2000° is reached. In the electric furnace (3500°) it fuses and boils. When water is poured upon it, much heat (CARE) is evolved:

$$CaO + H_2O \rightarrow Ca(OH)_2 + 16{,}000 \text{ cals.},$$

the lumps of lime crumbling and forming **slaked lime.** As more water is added, a creamy mush known as **milk of lime,** and finally **limewater,** is obtained. Quicklime exposed to the air (air-slaked-lime) combines not only with the water but with carbon dioxide as well, forming the carbonate. This may be demonstrated by breathing into limewater:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O.$$

**347. Uses of Limestone and Limes.**—The enormous quantities of limestone, quicklime and slaked lime consumed in industry are listed in Table 70.

TABLE 70. LIMESTONE CONSUMPTION[1] (U. S. A. 1939)

| INDUSTRY | QUICKLIME | SLAKED LIME |
|---|---|---|
| Agriculture (neutralizing acid soil) | 362,335 | 212,432 |
| Building (cement, mortar) | 1,000,498 | 649,919 |
| Glass (flux) | 148,102 | 1,780 |
| Metallurgy (form slag, $CaSiO_3$) | 748,853 | 48,656[2] |
| Paper (bisulfite dissolves wood lignin) | 464,224 | 37,986 |
| Tanning (curing hides) | 70,446 | 30,336 |
| Sugar refining (crystallizing sugar) | 18,831 | 12,454 |
| Water purification | 251,193 | 108,188 |
| Other uses | 518,305 | 171,302 |
| **Total** | **2,936,295**[2] | **1,318,053** |

**Mortar** is prepared by mixing slaked lime with quartz sand ($SiO_2$). The hardening process is due partly to the combination of lime with carbon dioxide in the air to form limestone, partly to the formation of colloidal calcium hydroxide, which gradually dries and "sets" like glue.

Mellor says: "In the mortars of some of the buildings of the ancient Romans, crusts of minute calcium carbonate crystals protect the inner cores of calcium hydroxide. An exposure of 2,000 years has not been sufficient to convert more than thin superficial layers of the colloidal hydroxide into carbonate."

**Cement** is made by heating limestone containing more than 10% clay to 3000° in a rotary kiln (Fig. 125), finely pulverizing, and adding less than 3% gypsum. The kilns, 8 to 13 feet high and 150 to 350 feet long, are supported on ball bearings and rotated three-quarters of a turn per minute. The finely pulverized

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[1] The limestone was not all made into quicklime. For example, the fertilizer industry used 5,495,260 short tons of limestone without further treatment. An additional 9,122,820 tons of limestone went for alkali, calcium carbide, filler, glass, paper pulping, refractories, road base, sugar refining and miscellaneous industries. The slaked lime in the last column came from the quicklime in the second column.

[2] These figures for metallurgy do not include the enormous quantities of raw dolomite ($CaCO_3$, $MgCO_3$) used in the steel industry for removing silica as slag.

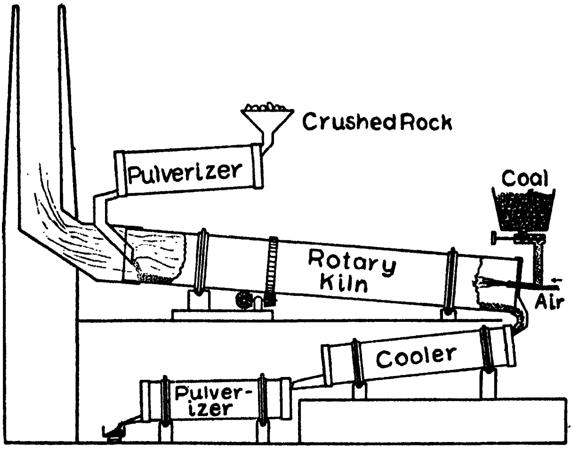
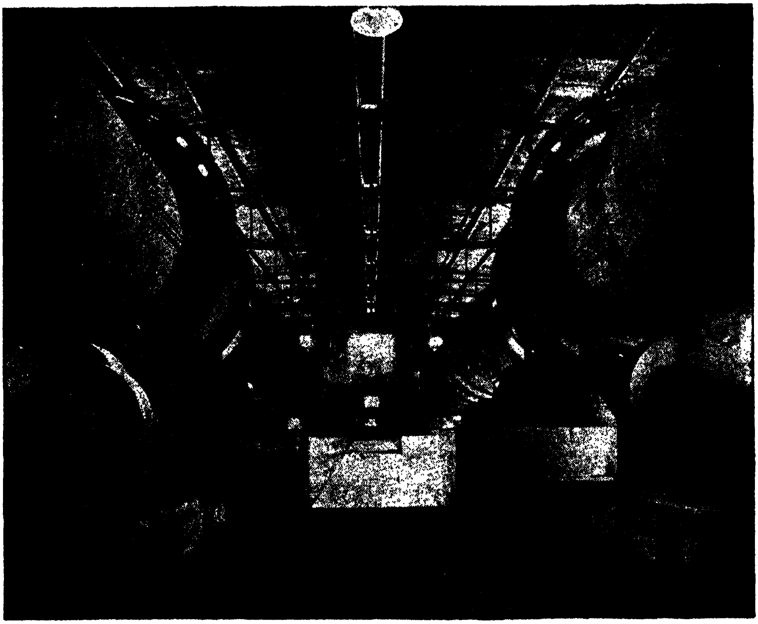


FIG. 125. Rotary kiln process.



*Courtesy of the Alpha Portland Cement Company.*

FIG. 126. Kiln building—looking towards discharge end. Kilns 344′ long by 11′3″ and 10′ in diameter. Morton Plant, Birmingham, Alabama.

cement is so fine (40,000 holes to the square inch) that 90% of it will pass through a sieve that holds water. This material has the property of hardening or setting under water (hydraulic cement). The gypsum is added to control the rate of setting. Portland cement is a common variety; it is similar to stone found at Portland, England.

There are nearly 700,000,000 sacks of cement and 200,000,000 paper bags of cement produced in the United States each year. There were 122,259,154 barrels (376 pounds each) made in the United States in 1939, of which Pennsylvania and California were the chief producers. (*a*) Roads, (*b*) buildings, (*c*) conservation (reclamation, water supply and sewerage) and (*d*) housing industries consumed nearly equal quantities.

The hardening of cement involves complex reactions not entirely understood. One set of reactions with calcium aluminate, $Ca_3(AlO_3)_2$, is

$$Ca_3(AlO_3)_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2Al(OH)_3.$$

The calcium hydroxide gradually crystallizes, cementing the particles of unchanged calcium silicate, while the aluminum hydroxide fills the interstices. **Concrete** is the mixture of cement, sand and crushed stone.

**348. Calcium Sulfate, $CaSO_4$.**—The dihydrate, $CaSO_4,2H_2O$ occurs abundantly as **gypsum.**

Varieties of gypsum are cleaving *selenite,* massive *alabaster,* and fibrous *satin spar* (for jewelry). An anhydrous form, *anhydride,* occurs in the Stassfurt salt beds. In 1939 the United States produced 3,227,737 short tons of gypsum of which 774,982 was for Portland cement (retards setting of cement); 75,091 for fertilizer particularly by the peanut-growers; 3,113,821 for plaster walls; and 110,395 for miscellaneous industries.

In cement, gypsum retards setting. In fertilizer it interacts with ammonium carbonate in the soil to form ammonium sulfate, which is retained in the soil longer because it is less volatile and more stable than the former.

**Plaster of Paris** $(CaSO_4)_2, H_2O$, so named from the Montmartre deposits near Paris where this cement was first produced, is manufactured by heating gypsum until about three-fourths of the water of hydration is expelled:

$$2CaSO_4, 2H_2O \rightleftarrows (CaSO_4)_2, H_2O + 3H_2O.$$

Too high a temperature must be avoided, else the product will become "dead-burnt" and will not readily set, unless the hydration is catalyzed by a substance such as alum.

### DEMONSTRATION 106. PLASTER OF PARIS

Materials: Evaporating dish, plaster of Paris, penny.

When plaster of Paris is mixed with water it sets to a white solid; for the dihydrate is formed as a network of interlacing fibrous crystals. A penny placed in the evaporating dish will leave its imprint on the plaster. Ordinary **base-coat** and **lath plaster** are varieties of plaster of Paris. Wall-board contains plaster between sheets of cardboard.

**349. Hard Waters.**—Water containing calcium sulfate is said to be **permanently hard.** It may be softened by adding sodium carbonate:

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4 \text{ (soluble).}$$

Calcium carbonate is precipitated, and sodium sulfate remains in solution, but salts of sodium and potassium do not render water hard.

**Temporarily hard waters** contain bicarbonates of calcium or magnesium, and are found in limestone and dolomite districts. Such waters may be softened by several processes.

(*a*) Heating to precipitate the magnesium and calcium as carbonates:

$$Ca(HCO_3)_2 \rightleftarrows H_2O + CO_2 \uparrow + CaCO_3 \downarrow .$$

(*b*) Adding limewater (Clark's process):

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O.$$
$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 + Mg(OH)_2 \downarrow + 2H_2O.$$

(*c*) **Permutit** process. Permutit is an artificial sodium silico-aluminate, which is employed in the form of a coarse sand (Fig. 127). Representing permutit by the formula $Na\bar{P}$, the following equation indicates the *exchange reaction* which occurs:

$$Ca(HCO_3)_2 + 2Na\bar{P} \rightarrow Ca\bar{P}_2 + 2NaHCO_3.$$

When the permutit has been in use for 12 hours, it is covered with a 10% solution of NaCl and allowed to remain out of use for another 12 hours, after which it is ready for further employment:

$$2NaCl + Ca\bar{P}_2 \rightarrow CaCl_2 + 2Na\bar{P}.$$

It is claimed that the life of a charge is over 20 years.

### DEMONSTRATION 107. HARD AND SOFT WATERS

**Materials: Four stoppered cylinders, soap solution, eye-dropper, limewater, 10 inch length of 6-mm. tubing, test glass, burner, 400 cc. beaker, column of permutit.**

**Upon blowing into limewater, calcium carbonate at first precipitates and then the precipitate dissolves to form calcium bicar-**

bonate. This last step is equation (a) above proceeding to the left. The water is now temporarily hard. Divide into four equal portions. Three of these will be softened by different methods (a) by boiling (b) by adding limewater and (c) by filtering through permutit. To each of the four samples of water in the stoppered cylinders, add 10 drops of soap solution. Shake, and demonstrate how hard water wastes soap. New York City would waste 200 tons of soap daily if its water were not softened.

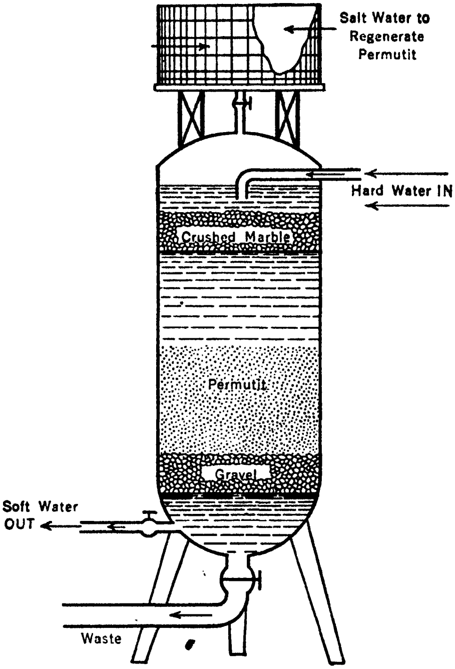


FIG. 127. Permutit process for softening water.

### STRONTIUM $^{87.63}_{38}\mathrm{Sr}$

**350. Occurrence and Properties.**—**Strontium,** from Strontian, a village in Scotland, occurs in a number of places in the United States as **celestite,** $SrSO_4$. There is also a carbonate ore, *strontianite.* However, American manufacturers of strontium nitrate for red flares, military signals and other pyrotechnic compounds have always imported the salts from Germany. Imports in 1939 were 5,645,935 pounds of mineral, 479,933 of nitrate, and 23,148 of oxide and carbonate.

The metal is prepared and its properties are the same as calcium.

**351. Strontium Compounds.**—In general, the compounds of strontium closely resemble those of calcium.

They are usually prepared from celestite or strontianite. Thus, celestite can be reduced to strontium sulfide by heating it with carbon:

$$SrSO_4 + 4C \rightarrow SrS + 4CO.$$

When strontium sulfide is treated with cupric oxide and water, a solution of strontium hydroxide is formed, cupric sulfide forming an insoluble residue:

$$SrS + CuO + H_2O \rightarrow Sr(OH)_2 + CuS\downarrow.$$

The transformation of strontium sulfate into strontium carbonate is an interesting application of the **solubility product** principle:

$$SrSO_4 + \underset{\text{excess}}{Na_2CO_3} \rightleftarrows SrCO_3 + Na_2SO_4,$$

for the reversible reaction can be driven to the right by using an excess of sodium carbonate, and boiling for some time until the equilibrium is established.

## BARIUM ${}^{137.36}_{56}Ba$

**352. Occurrence and Properties.**—**Barium** owes its name to a Greek word meaning *heavy*, for certain of its compounds are remarkable for their high density or specific gravity. Barium occurs principally as the mineral **barite** (heavy spar), $BaSO_4$. Germany and the United States produced over two-thirds of the world's barite, which was approximately a million metric tons in 1939. Missouri, Georgia and Tennessee accounted for about 80% of the domestic production. In England, considerable deposits of the carbonate, **witherite,** $BaCO_3$, exist.

The preparation and properties of metallic barium are similar to those of the other alkaline earth metals. On the other hand, pure barium is obtained as a vapor by heating barium oxide with aluminum or silicon *in vacuo.*

**353. Barium Compounds.**—Barium compounds form the link between the alkaline earth and alkali metal compounds. (1) For example, its carbonate, witherite, is considerably more difficult to decompose than is limestone, 1400° as compared with 910°. (2) Again, like the alkali metal hydroxides, barium hydroxide is much more soluble than magnesium, calcium or strontium hydroxides, the respective values being 3.36 g. for barium in contrast with 0.001, 0.17, and 0.4 g. per 100 g. of solution at 20° C. (3) Also, like the alkali metals, it forms a peroxide. Neither calcium nor strontium form peroxides, although $MgO_2$ is a commercial antiseptic and bleach. **Barium peroxide,** $BaO_2$, is obtained, when **barium monoxide,** BaO, is heated to low redness. The latter is prepared by strongly heating the nitrate.

Most barium salts are prepared from barite, $BaSO_4$. Since the latter is insoluble in water, it is first converted into the sulfide (by heating with carbon) or into the carbonate (by heating with sodium carbonate).

**Barium sulfate,** $BaSO_4$ is the most widely used of barium compounds. The native mineral barite (heavy spar) is characterized by its great density (sp. gravity 4.25). Because of this property, 125,560 short tons of ground barite was used in the United States in 1939 for weighting mud in oil-well drilling. Trinidad exports 25,000 tons for this purpose, and an equal amount of barite is recovered from waste muds each year. The most important single chemical made from barite is **lithopone,** 142,759 short tons of which was produced in 1939 in the United States.

$$\underset{\text{(solutions mixed)}}{BaS + ZnSO_4} \rightarrow \underbrace{BaSO_4 \downarrow + ZnS \downarrow}_{\text{lithopone}}$$

Paint containing lithophone has great covering power. Unlike lead paint, which forms black lead sulfide, lithopone does not darken in the presence of hydrogen sulfide, and is not poisonous. It is used extensively as a flat paint. A smaller market for lithopone is for compounding in linoleum and rubber. Precipitated barium sulfate is sold under the name of **permanent white** or *blanc fixe* for rubber goods, putty, oilcloth, linoleum and for weighting white paper.

### GROUP II-A: ANALYSIS AND USES

**354. Analysis of Group II-A.**—Magnesium compounds possess very few characteristic properties which can be used in identifying the element. The magnesium ion, $Mg^{++}$, is colorless, and the metal does not color the flame of a burner. However, magnesium may be precipitated as the phosphate, $NH_4MgPO_4, 6H_2O$, which is a white crystalline salt, yielding the pyrophosphate, $Mg_2P_2O_7$ at a high temperature. The metal may be precipitated with ammonium hydroxide *only* if other ammonium salts are absent.

For in the reactions

$$Mg(OH)_2 \rightleftarrows Mg^{++} + 2OH^- \qquad (a)$$

and

$$NH_4OH \rightleftarrows NH_4^+ + OH^- \qquad (b)$$

the presence of additional $NH_4^+$ (as for example $NH_4Cl$), will force reaction (b) to the left; this may decrease the $OH^-$ concentration so greatly that in (a) the product of the ion concentrations $(C_{Mg^{++}})(C_{OH^-})^2$ may be less than the solubility product (222); *i.e.*, no $Mg(OH)_2$ will precipitate.

### DEMONSTRATION 108. ANALYSIS OF GROUP II-A

Materials: Salt-shakers containing chlorides of the alkaline earth metals; 10 test glasses; solutions of $MgCl_2$, $SrCl_2$, $CaCl_2$, $BaCl_2$, $H_2S$-water, $(NH_4)_2S$, $(NH_4)_2CO_3$, $NH_4OH$, $NH_4Cl$, $Na_2HPO_4$, $K_2Cr_2O_7$, $CaSO_4$, $(NH_4)_2C_2O_4$ (oxalate), $CH_3COOH$ (acetic acid).

**Flame tests** are not given by beryllium or magnesium because their salts are not sufficiently volatile; but calcium shows brick-red, strontium crimson, and barium green.

$Ca^{++}$, $Sr^{++}$ and $Ba^{++}$ are not precipitated by hydrogen sulfide; but they are thrown down by ammonium carbonate as carbonates, which are readily soluble in acetic acid.

(a) $Ba^{++}$ is identified by adding potassium dichromate, which precipitates $BaCrO_4$, leaving $Ca^{++}$ and $Sr^{++}$ in solution.

(b) To half of the remaining solution, calcium sulfate is added: if $Sr^{++}$ is present, it will precipitate out as $SrSO_4$ after some minutes.

(c) To the other half of the filtrate from (a), ammonium oxalate is added: calcium oxalate precipitates.

This analytical procedure is intelligible in the light of the solubilities listed in Table 71.

TABLE 71. SOLUBILITIES OF SOME ALKALINE EARTH COMPOUNDS (Grams per 100 g. water at 18° C).

| | Hydroxide | Carbonate | Chromate | Sulfate | Oxalate | Chloride |
|---|---|---|---|---|---|---|
| Magnesium | 0.001 | 0.1 | 73 | 35.43 | 0.05 | 55.81 |
| Calcium | 0.17 | 0.0013 | 20 | 0.2 | 0.00056 | 73.19 |
| Strontium | 0.77 | 0.0011 | 0.12 | 0.011 | 0.0046 | 51.09 |
| Barium | 3.7 | 0.0023 | 0.00038 | 0.00023 | 0.0086 | 35.7 |

### 355. Industrial Compounds of Group II-A.—

TABLE 72. GROUP II-A: USES

| | |
|---|---|
| **Beryllium and its compounds** | **beryl, emerald (337).** |
| **Magnesium and its compounds** | **minerals (338); alloys (341); MgO, $MgCl_2$ and silicates (342); dolomite (343); $Mg(HCO_3)_2$ (349).** |
| Magnesium carbonate<br>magnesite<br>$MgCO_3$ | source of salts; ceramics; in rubber; polishing abrasive; heat insulator; metallurgical refractory; paint. |
| Magnesium carbonate (basic), magnesia alba $Mg(OH)_2$, $3MgCO_3$, $3H_2O$ | polishing for silver; toothpastes; cosmetics. |
| Dolomite<br>$MgCO_3$, $CaCO_3$ | building stone; refractory; source of lime for blast furnace. |
| Magnesium chloride<br>$MgCl_2$, $6H_2O$ | deliquescent material which makes salt sticky; fireproofing; sizing; ceramics; mixed with calcined magnesite, forms Sorrel cement. |
| Magnesium sulfate<br>Epsom salts<br>$MgSO_4$, $7H_2O$ | medicinal; fireproofing agent; sizing textiles. |
| **Calcium and its compounds** | **Ca (344); $CaCO_3$ (345); CaO and $Ca(OH)_2$ (346); $CaSO_4$ (349); $Ca(HCO_3)_2$ (349); phosphates (548).** |
| Calcium bisulfite<br>$Ca(HSO_3)_2$ | dissolves lignin from wood in paper-pulp industry. |
| Calcium carbide<br>$CaC_2$ | electric furnace product (504); source of acetylene for synthetic rubber, plastics, etc. |
| Calcium chloride<br>$CaCl_2$ (2 and $6H_2O$) | laying road dusts; refrigeration brine (F.P.—48°); surplus exists. |
| Calcium cyanamid<br>$CaCN_2$ | fertilizer, now obsolete as a source of nitrogen (504). |
| Calcium fluoride<br>fluorspar, $CaF_2$ | opaque glass; molten electrolytic bath in metallurgy; from Illinois and Kentucky. |
| Calcium hypochlorite<br>bleaching powder, chloride of lime<br>$CaCl(OCl)$ | textile bleaching; water purification; being replaced by $Cl_2$, NaClO, and $NaClO_2$. |
| Calcium phosphates | fertilizers; baking powder; medicines. |
| Calcium sulfide<br>CaS | depilatory in tanning and cosmetics; luminous paints. |
| **Strontium and its compounds** | **Sr, $SrSO_4$, and $SrCO_3$ (351).** |
| Strontium halides<br>$SrBr_2$ and $SrI_2$ | medicine. |

TABLE 72—*continued*

| | |
|---|---|
| Strontium hydroxide<br>$Sr(OH)_2$ | for refining sugar, forming strontium saccharate; lime is being substituted for it. |
| Strontium nitrate<br>$Sr(NO_3)_2, 4H_2O$ | pyrotechnics, railroad flares, military flares. |
| **Barium and its compounds** | **Ba (352); $BaO_2$, BaO, $BaSO_4$, and lithopone (353).** |
| Barium carbonate<br>$BaCO_3$ | manufacturing barium salts; neutralizing $H_2SO_4$ in dye industry; crown glass; rat poison; rubber ingredient. |
| Barium chlorate<br>$Ba(ClO_3)_2, H_2O$ | pyrotechnics for green flame; explosives. |
| Barium chloride<br>$BaCl_2, 2H_2O$ | soluble barium salt for chemical industry; purification of table salt by removing $Na_2SO_4$ and $MgSO_4$. |
| Barium fluoride<br>$BaF_2$ | antiseptic; enamels; embalming fluid. |
| Barium fluosilicate<br>$BaSiF_6$ | insecticide. |
| Barium hydroxide<br>$Ba(OH)_2, 8H_2O$ | absorbs carbon dioxide; a common hydroxide. |

## QUESTION REVIEW

### I. CHARACTERISTICS OF GROUP II-A (336)

1. Compare the alkali with the alkaline earth metals as regards (*a*) physical properties, (*b*) reaction with elements, (*c*) preparation; and for their compounds as regards (*d*) flame tests, (*e*) solubilities, (*f*) stability.
2. In which of the above properties does beryllium differ from the others? Account for this.

### II. BERYLLIUM (337).

3. Briefly describe the chemistry of beryllium.

### III. MAGNESIUM.

**a. History and occurrence (338). Metallurgy (339).**

4. Name four minerals containing magnesium, and state where they occur.
5. Discuss the world producers of magnesium.

**b. Properties (340). Uses (341). Compounds (342).**

6. Contrast the properties of magnesium and sodium.
7. Describe two important uses for magnesium.
8. Account for the formation of boiler scale.
9. What are the properties of magnesium oxide, and to what uses are these put in industry?

### IV. CALCIUM.

**a. Occurrence (343). Preparation and properties (344).**

10. How is calcium prepared? Why is so much prepared?

**b. Calcium carbonate, oxide, hydroxide (345–7). Limestone. Lime (347).**

11. Explain in terms of van't Hoff's Law why high temperature is used in a lime kiln. What else is done to drive the decomposition to completion?
12. Identify each of the following: slaked lime, limewater, endothermic reaction, fusible silicate, kiln, lime, limestone, mortar, concrete.

**c. Calcium sulfate (348).**

13. Describe the making of ordinary wall-plaster.

**d. Hard waters (349).**

14. Explain two methods for softening temporarily-hard water. Give equations.

V. STRONTIUM (350–1)

15. Explain the application of the solubility product principle in driving the reaction $SrSO_4 + Na_2CO_3 \rightarrow$ to completion.

VI. BARIUM (352–3).

16. What is the chief source of barium? Write two equations showing how this insoluble mineral is converted into the sulfide or carbonate.
17. In what respects does barium resemble lithium rather than the alkaline earth metals?
18. What advantages has lithopone over white lead?

VII. GROUP II-A: ANALYSIS AND USES (354–5).

19. Name the insoluble salts precipitated in the analysis for $Mg^{++}$, $Ca^{++}$, $Sr^{++}$, and $Ba^{++}$.
20. Why is magnesium hydroxide sometimes not precipitated by ammonium hydroxide if additional ammonium salts are present?
21. Name fifteen compounds of the alkaline earth metals and an important industrial use for each.

**Reading References:** Articles in the Appendix:

*Beryllium:* 43, 202, 229 and 236.

*Calcium:* 12, 26, 33, 69, 108, 115 and 310.

*Ceramics:* 33, 71 and 139.

*General:* 61, 140 and 218.

*Magnesium:* 106, 223, 322, 335 and 348.

# CHAPTER XXVII

## THE ZINC GROUP. GROUP II-B

**356. General Characteristics of Group II-B.**—The members of this group (Table 73) differ from the alkaline earth metals in much the same fashion that the I-B group differs from the I-A group (**314**). The Group II-B metals are heavier; they exhibit variable valence; and they have a greater tendency to form complex ions. Most of these differences can be attributed to the completed sub-shells which characterize the B sub-group elements in contrast to the incompleted sub-shells of the A sub-group elements.

TABLE 73. GROUP II-B

| Element | Atomic Weight | Atomic Number | Arrangement of Planetary Electrons | Density | Melting Point | Boiling Point |
|---|---|---|---|---|---|---|
| Zinc, Zn | 65.38 | 30 | 2–8–18–2 | 7.14 | 419.5° | 907° |
| Cadmium, Cd | 112.41 | 48 | 2–8–18–18–2 | 8.65 | 321° | 778° |
| Mercury, Hg | 200.61 | 80 | 2–8–18–32–18–2 | 13.6 | −38.9° | 357° |

Zinc, cadmium and mercury all have a valence of +2; in addition, cadmium forms CdCl and $Cd_2O$, and mercury forms $Hg_2^{++}$ (ous) compounds. As with group I-B, the least active metal is the heaviest member of the family; in fact mercury approaches the noble metals in its properties.

All three are relatively inactive metals. Zn and Cd tarnish, forming oxide and carbonate films; and readily reduce to the free state. Mercuric oxide and mercuric sulfide are actually decomposed into the elements upon heating; and mercuric hydroxide is so unstable that it cannot be prepared at room temperature. Zinc oxide is amphoteric, dissolving both in acids (forming $ZnCl_2$, for example) and hydroxides (forming sodium zincate $Na_2ZnO_2$). The hydroxides are relatively insoluble in water, while the sulfates are soluble (contrast group II-A). One striking and common property of Group II-B is the fact that their halides all hydrolyze to some extent (**595, e**).

## ZINC $^{65.38}_{30}\mathrm{Zn}$

**357. History and Occurrence.**—Zinc (German *zink*, probably akin to *zinn*, tin) did not come into general use until the nineteenth century.

An idol containing 87.5 per cent of zinc was found in a prehistoric settlement of Transylvania. Two bracelets filled with zinc have been discovered in the ruins of Cameros, which was destroyed about 500 B.C. **Brass,** an alloy of zinc and copper, was known to the Romans. Paracelsus, in the sixteenth century, showed that zinc is a metal. Zinc works were established at Bristol, England, in 1743. Zinc was first produced in the United States in 1835–1836, by John Hitz in the arsenal at Washington, D. C.

Zinc occurs chiefly in the following *minerals:*

| | |
|---|---|
| Zinc blende (German *blenden*, to dazzle), sphalerite, or black jack | $ZnS$ |
| Smithsonite | $ZnCO_3$ |
| Calamine | $Zn_2SiO_4, H_2O$ |
| Franklinite (New Jersey only) | $Zn(FeO_2)_2$ |
| Willemite (New Jersey only) | $Zn_2(FeO_2)_2$ |

The Joplin region, on the boundary between Oklahoma and Kansas, produced over half of the zinc in the United States in 1939. World production in 1939, chiefly from the United States (28 per cent), Germany (13 per cent), Canada (10 per cent) and Poland (7 per cent) was estimated at 1,645,000 metric tons.

**358. Metallurgy.**—75 per cent of the zinc in the United States is obtained by a smelting-distillation process, and 25 per cent by an electrolytic process; these percentages have not changed appreciably during the past decade.

**a. Distilling process.** Following concentration of the ore by flotation (290), it is converted into ZnO by roasting:

$$ZnCO_3 \text{ (smithsonite)} \rightarrow CO_2 \uparrow + ZnO,$$
$$2ZnS \text{ (zinc blende)} + 3O_2 \rightarrow 2SO_2 \uparrow + 2ZnO.$$

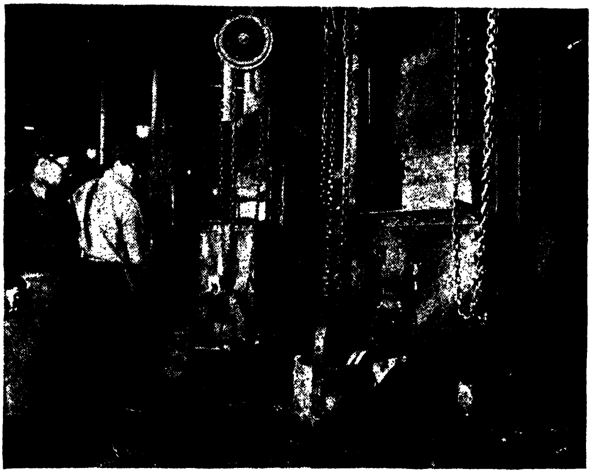
The zinc oxide is then reduced with carbon by the **Belgian process.**

A mixture of the oxide and coal is placed in tube-shaped retorts of fire-clay, 3 to 5 feet long and 10 inches internal diameter. A conical earthenware receiver terminating in an iron nozzle is luted to the open end of each retort, and 200 to 400 of the retorts are arranged in several tiers in a furnace and heated by means of gas. At a high temperature (about 1,400°) the oxide undergoes reduction, the carbon monoxide burning at the nozzle:

$$ZnO + C \rightarrow Zn \uparrow + CO \uparrow.$$

As the temperature is above the boiling point of zinc (907°), the **metal passes off as vapor** and condenses for the most part in the receivers, while zinc dust and zinc oxide collect in the iron nozzles. The liquid zinc is removed from time to time and cast into zinc slabs called **spelter** (Fig. 128).

The impure spelter may be purified by distillation. The mineral zinc blende usually contains traces of sulfides of cadmium, iron, arsenic, and gallium; these elements accordingly are found in impure commercial zinc. Lead too is present in the ore, but this has usually been removed by selective flotation. Cadmium distills off before the zinc (see Table 73).



*Courtesy of the New Jersey Zinc Company*

FIG. 128. Last step in the production of metallic zinc by the vertical retort smelting process. Here, the condensers are being tapped and the molten zinc will be poured from these ladles into slab molds for cooling.

The New Jersey ores, representing about 15 per cent domestic production, can be mixed directly with coal, but generally they are heated in a current of air, which sweeps zinc oxide out of the furnace into large canvas bags.

**b. Electrolytic process.** The first step is similar to the foregoing method. ZnO is prepared by roasting the ore (in the case of the sulfide ore some $ZnSO_4$ is also formed). The oxide is then converted into $ZnSO_4$ by treatment with dilute sulfuric acid. Electrolysis of this, between lead anodes and sheet-aluminum cathodes, gives a plating of Zn on the cathodes which are removed, melted and cast. Sulfuric acid, formed at the same time around the lead anode, can be used again to dissolve another charge of zinc oxide. Today electrolysis is applied not only to copper-zinc and lead-zinc sulfides, but to other zinc ores as well.

**359. Properties of Zinc.**—Zinc is a silvery white crystalline metal, which has a density of 7.14; it melts at 419.4°, boils at 907°, and at 120°–150° it is malleable and ductile, but becomes brittle again at 200°–300°. When melted and poured slowly into water, it forms granulated zinc. Cast zinc is malleable and ductile at temperatures above 100°. Wrought zinc is ductile even at somewhat below room temperature.

Dry air or air free from carbon dioxide does not tarnish zinc at ordinary temperatures; but moist air oxidizes the surface, a grayish coating of basic carbonate being formed. The film greatly retards further corrosion of the zinc. At temperatures above approximately 750° zinc burns with a greenish-white flame, forming finely divided zinc oxide. Zinc dust sometimes ignites spontaneously, and the dust suspended in air may explode. Commercial zinc interacts readily with dilute acids, forming hydrogen, but pure zinc dissolves very slowly (explain). Zinc interacts with the hot caustic alkalies, hydrogen being formed, as well as a zincate:

$$Zn + NaOH + H_2O \rightarrow NaHZnO_2 + H_2 \uparrow .$$

Zinc is usually more active than the heavy metals, and therefore displaces them from solutions of their salts. Iron, manganese and nickel are exceptions. We have already seen that zinc may be deposited electrolytically (**358**).

**360. Uses.**—Zinc has innumerable uses. Sheet zinc serves for roofs, gutters, piping, bathtubs, wash-boards, etc. Zinc shavings and dust are used as a precipitant of gold and silver from cyanide solution. Zinc is cast in the form of ornaments, statues, and blocks for hats. The metal is used to prepare zinc oxide (a white pigment), in batteries, as a reducing agent, and for generating hydrogen. Iron is usually **galvanized** by dipping the clean metal into a bath of fused zinc, the latter metal furnishing a protective coat, which prevents rusting. By covering iron with zinc dust and then heating, **sherardized iron** is obtained. Vast quantities of zinc are used in the manufacture of alloys, such as brass, antifriction (white) metal, Babbitt metal, die-castings, and German or nickel silver. **Brass** contains from 18–40 per cent of zinc (see Copper). Certain antifriction metals contain from about 75–85 per cent of zinc, together with copper, and either antimony or tin. **German silver** is an alloy of zinc, nickel and copper (no silver).

**361. Compounds of Zinc.—Zinc oxide,** ZnO, is manufactured on a large scale by burning the vapor of the metal:

$$2Zn + O_2 \rightarrow 2ZnO + 168{,}700 \text{ cals.}$$

The zinc vapor is obtained (1) by the burning of roasted or other oxide ore with carbonaceous material (American Process) or (2) by boiling zinc metal (French Process). The oxide is white while cold, but yellow while hot; it is known as **zinc-white** or **Chinese white,** and is used in paint (not darkened by hydrogen sulfide) and as an activating and reinforcing pigment in automobile tires.

**Zinc hydroxide,** $Zn(OH)_2$, may be obtained as a white flocculent precipitate by treating a solution of a zinc salt with an alkali. The compound is almost insoluble in water, but is readily soluble in acids and in an excess of the alkalies.

### DEMONSTRATION 109. AMPHOTERIC ZINC HYDROXIDE

Materials: Three test glasses, solutions of $ZnCl_2$, NaOH, and HCl.

$Zn(OH)_2$ is **amphoteric,** *i.e.*, it behaves both as an hydroxide and an acid:

$$Zn^{++} + 2OH^- \rightleftarrows Zn(OH)_2 \rightleftarrows 2H^+ + (ZnO_2)^=.$$

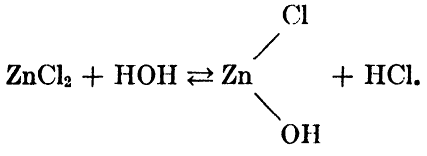
(*a*) Like an hydroxide it reacts with acids to give a salt and water:

$$Zn(OH)_2 + 2HCl \rightarrow \underset{\text{zinc chloride}}{ZnCl_2} + 2H_2O.$$

(*b*) Like an acid it reacts with hydroxides to give a salt and water (rewriting $Zn(OH)_2$ as $H_2ZnO_2$):

$$H_2ZnO_2 + 2NaOH \rightarrow \underset{\text{sodium zincate}}{Na_2ZnO_2} + 2H_2O.$$

**362. Zinc Chloride, $ZnCl_2$.**—Zinc chloride may be formed by treating zinc oxide ore with HCl. The solution is purified and evaporated to commercial salt. Zinc chloride is very deliquescent. Since the chloride is a salt of a less active metal, it tends to undergo partial hydrolysis:



$$ZnCl_2 + HOH \rightleftarrows Zn\begin{matrix}\diagup Cl\\ \diagdown OH\end{matrix} + HCl.$$

It is used in the solid state as a caustic. Its solution is injected into wood, such as railway sleepers, as a poison to prevent decay. A hot solution of the salt dissolves cellulose, and is used in making parchment paper.

## CADMIUM $^{112.41}_{48}Cd$

**363. Occurrence and Preparation.**—Cadmium (Greek *cadmia*, calamine) was discovered in zinc ores by Stromeyer (1817). The metal occurs as the sulfide (CdS) in the somewhat rare mineral **greenockite** (Greenock, Scotland). Its chief industrial source, however, is zinc ores; zinc blende, for instance, averages 0.2 per cent of cadmium. Also flue dusts from zinc smelter chimneys are caught and worked for cadmium.

**In zinc distillation** (358, a) the cadmium volatilizes first, with more or less zinc dust, as a brownish powder. Subsequent repeated distilling with carbonaceous material yields pure cadmium. **In the electrolytic process for zinc** (358, b) cadmium may be precipitated from the crude zinc sulfate electrolyte by adding zinc dust. Or the distilled concentrate may be dissolved and electrolyzed.

In 1937 production of cadmium was 950 tons, of which 52 per cent came from the United States. The zinc producing countries (357) are, naturally, the cadmium producers.

**364. Properties and Uses.**—Cadmium is a silver-white, fibrous metal, having very much the appearance of zinc. It melts at 321°, boils at 778°, and has a density of 8.65. The metal is harder than tin and is malleable and ductile. It interacts with dilute acids, yielding hydrogen, but is less active than is zinc. Cadmium is less easily oxidized than zinc. When heated in air, it burns to form the brown oxide, CdO.

Cadmium produced in 1940 found its way into the following products: electroplating, 1868 tons; bearing alloys, 573 tons; pigments and chemicals, 853 tons; miscellaneous, 310 tons. Bearing metals often contain Cd-Pb or Cd-Bi. Pigments are CdS, yellow and red lithopones. The latter three uses are becoming increasingly important. In a nation cut off from tin (*e.g.*, Germany) cadmium is substituted in solders and plating.

**365. Compounds of Cadmium.**—**Cadmium oxide**, CdO, is produced as a brown powder by oxidizing the metal. The **hydroxide**, $Cd(OH)_2$, may be obtained as a white precipitate by treating a solution of a cadmium salt with a caustic alkali; it is not soluble in excess of the reagent, and is not amphoteric in character.

The **sulfide**, CdS, is produced as a yellow precipitate by treating a solution of a cadmium salt with hydrogen sulfide. The salt is practically insoluble in dilute hydrochloric or sulfuric acid. Commercially, it is the most important salt of cadmium, being known as "cadmium yellow," and is used as a pigment, similar to lithopone. When properly prepared, it is one of the most permanent pigments known. The sulfide is used on a large scale to give color and luster to glass and porcelain.

## MERCURY $^{200.6}_{80}Hg$

**366. Occurrence.**—**Mercury,** commonly called **quicksilver,** was known to the Greeks as early as 400 B.C.; and during the Middle Ages it excited the curiosity of the alchemists.

The metal was named after Mercury, the messenger of the gods; and the symbol Hg comes from the Latin word *hydrargyrum* (Greek, water-silver).

Mercury occurs in a small quantity in the **native** state; but the chief source of the metal is the sulfide ore **cinnabar,** HgS.

Of the 4590 tons produced in 1937, Italy accounted for 2308 and the United States (California) 569 tons. Spain, which in 1935 produced half the mercury of the world, is accredited with only 987 tons in 1937, Italy having temporarily acquired the Spanish market. Spain was back into high production by 1941. Production figures are usually given in flasks, a flask of mercury weighing 76 pounds. During 1939–41 there was a meteoritic rise in the production of mercury for fulminate detonators ($Hg(ONC)_2$) and the price of mercury rose from $20 a flask to $200 for the first months of the war. Although deposits in British Columbia were discovered only in 1937, they yielded 260 tons of mercury during the first half of 1940. In Mexico, 254 tons was produced in 1939, mostly in crude stills by the peasants.

**367. Metallurgy.**—Mercury is obtained from cinnabar by heating the mineral either in furnaces or retorts, largely the former. When the ore is heated in furnaces, it is usually exposed to the direct action of the flame, the metal being obtained by a combined roasting and distillation:

$$HgS + O_2 \rightarrow Hg + SO_2.$$

The volatile products, including the mercury vapor, are drawn into condensing chambers, and the mercury obtained as a liquid. This method is the one most generally employed. When the ore is heated in closed retorts, lime may be added:

$$2HgS + 2CaO \rightarrow 2CaS + 2Hg + O_2.$$

A temperature of about 360° is sufficient to decompose cinnabar and to volatilize the mercury. The metal may be purified by distillation *in vacuo*, or by treatment with dilute nitric acid. In the laboratory it is often freed from more active metals by allowing it to fall through nitric acid in the form of small globules.

**368. Properties and Uses.**—Mercury is a silver-white liquid with a density of 13.6 at 0°; it freezes at $-38.89°$ and boils at 357°. Even at ordinary temperatures, mercury evaporates slowly. The vapor of mercury is colorless and consists of monatomic molecules (Hg).

Langmuir of the General Electric Company invented a "mercury vapor pump" for producing vacuum pressures of $10^{-6}$ mm. In principle it operates like an ordinary water suction pump but uses mercury vapor instead.

Both the vapor and the finely divided substance are poisonous, so that the production of mercury is attended by danger of **salivation**, or **mercurial poisoning.** *When the vapor of mercury is heated well above its boiling point, it conducts electricity* (mercury lamps). Mercury forms amalgams quite readily with most of the other metals. The Weston standard cell utilizes this property (Fig. 129).

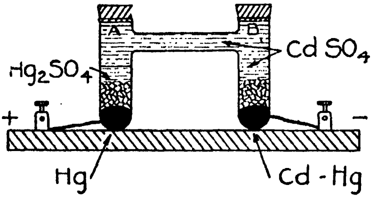


FIG. 129. The Weston standard cell. This delivers the exact voltage of 1.0183 V. at 20°.

Chemically, mercury is not an active metal, approaching the "noble metals" in its properties. When heated in air almost to its boiling point, it becomes coated with mercuric oxide, which is unstable; it unites with sulfur and with chlorine, is insoluble in dilute hydrochloric and sulfuric acids, but interacts with nitric acid to form mercurous or mercuric nitrate, and with hot concentrated sulfuric acid to form mercuric sulfate and sulfur dioxide.

Peacetime uses for mercury in the United States are: mercurial salts (calomel, corrosives, oxides, organic mercurials) 45 per cent; mechanical adaptions such as meters, barometers and so forth, 12 per cent; electrolytic cells such as in the Nelson process for chlorine and lye (**139**) 8 per cent; vermillion 6 per cent. Amalgamation of gold and dental amalgams consume only small quantities. Mercury-vapor turbines, which a decade ago presaged an important use for the metal, have not been satisfactory in practice. Mercury fulminates, as detonators, account for only 5 per cent in peacetime, but in war the demand surpasses all other uses for mercury. For example, England placed a single order for 10,000 flasks (380 tons) early in 1940.

**369. Mercurous Compounds.**—Mercury forms two well defined series of compounds, the mercurous ($Hg_2^{++}$) and the mercuric

($Hg^{++}$) compounds. **Mercurous chloride, or calomel,** $Hg_2Cl_2$ is the most important mercurous compound. As a rule, mercurous salts are formed by the action of mercury on mercuric salts, and calomel is no exception:

$$HgCl_2 + Hg \rightleftarrows \underset{\text{calomel}}{Hg_2Cl_2}.$$

The salt is obtained as a white crystalline sublimate. It also may be prepared by the interaction of a solution of a mercurous salt and a soluble chloride:

$$2HgNO_3 + 2HCl \rightarrow Hg_2Cl_2 \downarrow + 2HNO_3.$$

The salt is practically insoluble in water, slowly affected by light (see Halides of Silver), mercuric chloride being formed; and is blackened by contact with ammonia, a mixture of Hg (black) and $Hg(NH_2)Cl$ being produced.

Calomel has long been used in medicine for the stimulation of secretory organs. It is best administered in very small doses with sodium bicarbonate to lower its solubility in the acidic gastric juice.

**370. Mercuric Compounds.**—

**Mercuric chloride, or corrosive sublimate,** sometimes called bichloride of mercury, $HgCl_2$, is prepared by heating a mixture of mercuric sulfate and sodium chloride, a crystalline sublimate being formed:

$$HgSO_4 + 2NaCl \rightarrow HgCl_2 + Na_2SO_4.$$

Mercuric chloride is moderately soluble in cold water, but much more soluble in hot water. It is a violent poison, affecting the kidneys. It is coagulated by proteins; hence the white of egg is used as antidote for the poison. A solution of corrosive sublimate is a powerful antiseptic.

**Mercuric fulminate,** $Hg(ONC)_2$, is prepared by treating mercury with strong nitric acid and alcohol. The salt is used as a detonator for high explosives, and to some extent in small-arms ammunition. The discovery of mercuric fulminate led to the invention of the percussion cap, which displaced the old flintlock. The fulminate is still the most-used detonator for gunpowder and high explosives. It is often mixed with other substances, such as powdered glass, potassium chlorate, picric acid, trinitrotoluene etc.

### DEMONSTRATION 110. CURIOUS MERCURIC SALTS

Materials: Three test glasses, 3 test-tubes, burner, solutions of $Hg(NO_3)_2$, KI, KCNS; solid $Hg(NO_3)_2$, KI, NaOH, dextrin; mortar and pestle, 6-inch square of asbestos, few drops of Hg in test-tube, funnel, filter paper.

Mercuric compounds tend to form a number of colored allotropic forms. **Mercuric iodide,** $HgI_2$, is precipitated from solution or formed by grinding the solid reactants in a mortar. Coated on a square of asbestos, the brilliant red $HgI_2$ turns bright yellow above 128°; upon cooling down, the red variety returns when the powder is rubbed or scratched. It is used in medicine. **Mercuric oxide,** HgO, obtained by warming mercury, is red; but heating a mixture of sodium hydroxide and mercuric nitrate forms a yellow modification. **Pharaoh's serpents** are formed when mercuric thiocyanate, $Hg(CNS)_2$, precipitated from solution, is kneaded with dextrin into little cones; they will burn when dry, leaving a voluminous ash.

## GROUP II-B. GENERAL

### 371. Analysis of Group II-B.—

### DEMONSTRATION 111. ANALYSIS OF GROUP II-B

Materials: Ten test glasses, solutions of $Zn(NO_3)_2$, $HgNO_3$, $Hg(NO_3)_2$, $Cd(NO_3)_2$, HCl, $H_2S$, $(NH_4)_2S$, aqua regia, $NH_4OH$, $CuSO_4$, $HNO_3$, (KCN; CARE: to be handled in alkaline solution, and by the instructor); filter paper, filter-rack with funnels, stirring rods.

In the routine qualitative analysis, **mercurous chloride** is precipitated upon adding hydrochloric acid to a solution containing $Zn^{++}$, $Cd^{++}$, $Hg_2^{++}$ and $Hg^{++}$ ions. The $Hg_2Cl_2$ is treated with ammonium hydroxide (which dissolves AgCl, if present), forming a black mixture:

$$Hg_2Cl_2 + 2NH_4OH \rightarrow HgNH_2Cl \downarrow + Hg \downarrow + NH_4Cl + 2H_2O.$$

When $H_2S$ is bubbled into the filtrate, which now contains $Zn^{++}$, $Cd^{++}$, and $Hg^{++}$, black HgS and yellow CdS are precipitated. The latter is soluble in dilute nitric acid. The black **mercuric sulfide** is converted into mercuric chloride, $HgCl_2$, by boiling in aqua regia. Treated with stannous chloride, two distinctly consecutive reactions occur, a white precipitate of $Hg_2Cl_2$ being first formed, followed by reduction of the calomel to mercury when the reagent is used in excess:

$$(1)\ 2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 \downarrow + SnCl_4,$$

$$(2)\ Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg \downarrow + SnCl_4,$$

the mercury being obtained in the form of small gray globules.

If $Cu^{++}$ is present, the **cadmium** must be isolated from it. This is accomplished by forming cyanide complexes (323).

**Zinc sulfide** is precipitated later in the analysis by the use of ammonium sulfide. It is white, soluble in strong acids, but practically insoluble in acetic acid and dilute alkalies When a zinc compound is heated on charcoal, the resulting oxide is yellow, but turns white upon cooling; heated with cobalt nitrate, it turns green.

All of the ions $Zn^{++}$, $Cd^{++}$, $Hg_2^{++}$, and $Hg^{++}$ are colorless. The salts do not give distinct flame tests as do the members of Groups I-A and II-A.

372.—

TABLE 74. USES FOR GROUP II-B COMPOUNDS

| | |
|---|---|
| **Zinc and its compounds** | **Zn, alloys (360); $ZnO$, $Zn(OH)_2$ (361); $ZnCl_2$ (362); $ZnS$ in lithopone (353).** |
| Zinc ammonium chloride $ZnCl_2, 3NH_4Cl$ | dry cells; welding and soldering flux. |
| Zinc carbonate Smithsonite $ZnCO_3$ | pigment, rubber ingredient, ceramics, cosmetics, medicine; basic carbonate $ZnCO_3, xZn(OH)_2$ also used. |
| Zinc stearate $Zn(C_{17}H_{35}COO)_2$ | mixed with $ZnO$ and zinc palmitate as a cosmetic and medical powder. |
| Zinc sulfate, white vitriol $ZnSO_4, 7H_2O$ | poisonous; preserving hides, mordant, ceramics, galvanizing, manufacture of zinc salts, eye wash. |
| **Cadmium and its compounds** | **Cd, alloys (364); $CdO$, $Cd(OH)_2$, $CdS$, lithopones (365).** |
| Cadmium halides $CdBr_2$ and $CdI_2$ | photography; engraving. |
| Cadmium red | about 90% $CdS$, 10% $CdSe$; expensive maroon pigments. |
| Cadmium sulfate $3CdSO_4, 8H_2O$ | eye wash; construction of cells of standard electromotive force, *i.e.*, normal Cd cell. |
| **Mercury and its compounds** | **Hg (368); calomel (369); corrosive sublimate, fulminate, $HgI_2$, $HgO$, Pharaoh's serpents (370).** |
| Citrine ointment | mixture of mercuric nitrate and lard. |
| Mercuric nitrate $Hg(NO_3)_2$ | roughens rabbit's fur (carroting) so hair will adhere for making felt hats. |
| Mercuric sulfate mercury bisulfate $HgSO_4$ | white powder; hydrolyzed to $HgSO_4, 2H_2O$; medicine; catalyst; extracting gold and silver; manufacture of $HgCl_2$. |
| Mercuric sulfide cinnabar $HgS$ | ore of mercury; vermillion pigment, an expensive pigment known to the ancients, importance now waning. |
| Mercurous nitrate $HgNO_3, H_2O$ | preparation of mercurous compounds. |
| Ammono mercuric chloride $HgNH_2Cl, 2H_2O$ | white precipitate; medicine. |
| Mercurous iodide, yellow mercurous iodide $Hg_2I_2$ | darkens in daylight; medicine. |

## QUESTION REVIEW

### I. GENERAL CHARACTERISTICS OF GROUP II-B (356).

1. State three properties in which the B elements differ from the A elements in Groups I and II. Explain in terms of planetary structure.
2. Discuss the properties of the oxides and hydroxides of Group II-B. What important fact is associated with their halides?

### II. ZINC (357–362).

3. Where, and by what processes, is zinc obtained? Why is one of the processes named "distillation"?
4. State some of the physical and chemical properties of zinc. Of its alloys.
5. Show by equations everything that occurs when sodium hydroxide is added to a solution of zinc chloride.

### III. CADMIUM (363–365).

6. Account for the fact that zinc producers are also cadmium producers.
7. What is the chief use for cadmium? Name two other uses.

### IV. MERCURY (366–370).

8. What is the difference between the metallurgy of ZnS and HgS? Why was production enormously increased in 1940?
9. Contrast some of the chemical properties of mercury with those of zinc. With those of barium.
10. Outline the preparation, properties and uses of calomel. Of corrosive sublimate.
11. Describe some demonstrations with mercury compounds.

### V. GENERAL PROPERTIES OF GROUP II-B.

#### a. Analysis of Group II-B (371).

#### b. Uses for Group II-B Compounds (372).

12. Explain how the following ions may be separated from one another: (1) $Hg_2^{++}$ from the other members of Group II-B, (2) $Cu^{++}$ from $Cd^{++}$, (3) $Hg^{++}$ from $Cd^{++}$, (4) $Zn^{++}$ from $Hg_2^{++}$, and (5) $Zn^{++}$ from $Hg^{++}$.

13. What occurs when stannous chloride is added to a solution of mercuric chloride?
14. From your knowledge of their chemical separation, which would you suppose has the larger solubility product constant, ZnS or CdS?
15. Give an industrial use for ten compounds which contain a member of Group II-B.

**Reading References:** Articles number 15, 61 and 64 in the Appendix.

## CHAPTER XXVIII

## THE RARE EARTHS, THE ALUMINUM FAMILY

### GROUP III-A. THE RARE EARTH METALS

**373. The Rare Earth Metals.**—The fact that there were only two empty spaces in the periodic table between barium (at.wt. 137) and thallium (at.wt. 182) must have caused Mendeléeff and his contemporaries considerable concern. The only elements fitting into Group III-A were two rare earth-like oxides, ceria and yttria, which had been known since the beginning of the nineteenth century. Today, on the basis of modern planetary structure and further examination of crude ceria and yttria, 15 elements qualify for position number 57 in the periodic table. To them has been given the name **rare earths.**

Why their number is limited to 15 is at once apparent from Table 75.

TABLE 75. ELECTRONIC ARRANGEMENT OF ELEMENTS 55–73

| Quantum levels | | 1s | 2s, 2p | 3s, 3p, 3d | 4s, 4p, 4d | 4f | 5s, 5p, 5d | | 6s |
|---|---|---|---|---|---|---|---|---|---|
| Cesium | 55 | 2 | 8 | 18 | 18 | — | 8 | 0 | 1 |
| Barium | 56 | 2 | 8 | 18 | 18 | — | 8 | 0 | 2 |
| then follow the 15 rare-earth metals | | | | | | | | | |
| Lanthanum | 57 | 2 | 8 | 18 | 18 | 0 | 8 | 1 | 2 |
| Cerium | 58 | 2 | 8 | 18 | 18 | 1 | 8 | 1 | 2 |
| etc. down to | | | | | | to | | | |
| Lutecium | 71 | 2 | 8 | 18 | 18 | 14 | 8 | 1 | 2 |
| followed by elements which are not rare earths | | | | | | | | | |
| Hafnium | 72 | 2 | 8 | 18 | 18 | 14 | 8 | 2 | 2 |
| Tantalum | 73 | 2 | 8 | 18 | 18 | 14 | 8 | 3 | 2 |

The 4f position is filled up, consecutively from 0 to 14, by the rare earths. Their outer three shells are the same, therefore their chemistry is alike. They have, for example, a common valence of +3.

Cerium is the only exception to the rule; it forms both cerous ($Ce^{+3}$) and ceric ($Ce^{+4}$) compounds. In this latter valence cerium resembles thorium, and has been included in Group IV for this reason. Ceric sulfate, $Ce(SO_4)_2$ is a powerful oxidizing agent used in volumetric analysis (**386**).

The rare earths must be thought of as being quite active metals, *e.g.*, like calcium. Thus they burn in air to form oxides; the oxides dissolve in water, often with hissing, like quicklime; and the hydroxides which are formed are alkaline to litmus.

**Cerium sub-group** is the term applied to the elements with atomic numbers 57 to 62; these elements are usually associated with cerium in **monazite sands.** This sand contains phosphates of the cerium sub-group, including about 30 per cent cerium oxide and 2–28 per cent thorium oxide. It is mined, chiefly in India, for its thorium oxide (**386**).

**Yttrium sub-group** is the name given to the remaining rare earths, numbers 63 to 71. These are found associated with yttrium in the silicate mineral **gadolinite.**

Some of the rare earths are really quite abundant, *i.e.*, cerium and neodymium are found in certain localities in quite high concentrations. Other rare earths are really rare, *i.e.*, elements numbers 71, 68, 67, 69, 65, 63, and 61. Number 61, illinium, was discovered by X-ray analysis at the University of Illinois by B. S. Hopkins in 1926.

Owing to the extraordinary chemical similarity of the members of the rare earths and to the fact that they are associated in nature, it is very difficult to separate and prepare them in the pure state. In certain cases many hundreds of fractional crystallizations have been carried out to obtain a pure compound.

**374. Other Group III-A Elements.**—**Yttrium** is often spoken of as a rare earth element, despite its location in the periodic table. **Scandium** was one of the elements predicted by Mendeléeff (**285**). **Actinium** is the fountain-head of a radioactive series (**251**).

## THE ALUMINUM FAMILY

**375. Characteristics of Group III-B.**—Boron, like beryllium, forms a very small ion. For this reason it behaves more as a nonmetal than as a metal, just as beryllium was found to differ from the active metals in Group II-A (**336**). Boron will therefore be taken up in a separate chapter along with silicon, whose chemistry it resembles to a considerably greater extent than it does aluminum.

The remaining elements in Group III-B are called **the aluminum family** and include aluminum, gallium, indium, and thallium (Table 76).

TABLE 76. THE ALUMINUM FAMILY

| Element | Atomic Weight | Atomic Number | Arrangement of Planetary Electrons | Density | Melting Point | Boiling Point |
|---|---|---|---|---|---|---|
| Aluminum, Al | 26.97 | 13 | 2-8-3 | 2.7 | 660° | 1800° |
| Gallium, Ga | 69.72 | 31 | 2-8-18-3 | 5.91 | 29.75° | 2000° |
| Indium, In | 114.76 | 49 | 2-8-18-18-3 | 7.3 | 155° | >1450° |
| Thallium, Tl | 204.39 | 81 | 2-8-18-32-18-3 | 11.85 | 303.5° | 1650° |

The last three elements of the family are of little importance, although they occur so widely as impurities in zinc blendes (one ore discovered in 1939 contains 0.2 per cent gallium) that they could be produced in substantial quantities if there were sufficient demand. Research has failed thus far to produce any large outlet. **Gallium** was discovered by Lecoq de Boisbaudran four years after its prediction by Mendeléeff (**285**). Germany produced 20 pounds, worth $36,000, in 1939, chiefly for high temperature thermometers, since gallium is liquid from room temperature to 1600°. **Indium** (indigo-blue spectral lines) was discovered by Reich and Richter (1863); and though various uses for it have been proposed, it still sells (1941) for $20 an ounce. **Thallium** (Greek, green twig), discovered by Crookes (1861), has a bright-green spectrum, and is more abundant than the other two members.

In keeping with their analogues in the other B sub-groups, these elements exhibit variable valence, $Ga^{+2}$ and $Ga^{+3}$; $In^{+1}$, $In^{+2}$ and $In^{+3}$; and $Tl^{+1}$ and $Tl^{+3}$. Trivalent salts of Ga and In are very similar to the corresponding aluminum salts, *e.g.*, $Ga(OH)_3$ and $In(OH)_3$ are amphoteric like $Al(OH)_3$. On the other hand, $Tl(OH)_3$ does not act as an acid; *i.e.*, it does not form a compound corresponding to $NaAlO_2$. In 1939 Iln in Moscow found that thallous nitrate, $TlNO_3$, fed in small doses to sheep causes them to molt like birds.

The remainder of the chapter will be devoted to the **chemistry of aluminum.**

### ALUMINUM $^{26.97}_{13}Al$

**376. History and Occurrence.**—Aluminum (Latin *alumen*, alum) was first prepared by Oersted in 1825; and Sainte Claire Deville devoted four years of his life to preparing it in fairly large amounts (1854).

Aluminum is widely distributed, constituting 8 per cent of the earth's crust, although most of it is present as silicates, from which the metal cannot be profitably extracted, *e.g.*, clays from the weathering of feldspars (**307**), feldspars, and mica. The ore from which aluminum is obtained is **bauxite,** from the village of Les Baux, France. This is a mixture of the aluminum hydrates

$Al(OH)_3$ and $Al(O)OH$, usually containing iron oxide, some titanium oxide and not over 5 per cent silica. The total aluminum content, calculated as $Al_2O_3$, is usually over 50 per cent.

Production statistics for 1938 are given in Table 77. For obvious reasons few figures have been released since then. It is interesting to note that the United States, which has fairly large supplies of bauxite in Arkansas, imported 55 per cent of its bauxite from Dutch Guiana in 1940.

TABLE 77. ALUMINUM PRODUCTION (1938), PRINCIPAL COUNTRIES ONLY

(in metric tons)

| OF BAUXITE ORE | | OF FINISHED ALUMINUM | |
|---|---|---|---|
| France | 682,440 | Germany | 161,100 (28%) |
| British Guiana | 382,409 | United States | 130,100 (23%) |
| Dutch Guiana | 377,213 | Canada | 66,000 |
| United States | 315,906 | France | 45,300 |
| USSR | 250,000 | USSR | 43,800 |
| (Germany) | 19,703 | | |
| **World Production** | **3,849,000** | **World Production** | **578,000** |

Aluminum occurs also as the oxide, $Al_2O_3$, in **corundum,** of which the precious stones, ruby and sapphire, and the abrasive, emery, are varieties. The mineral **cryolite,** $AlF_3$, $3NaF$, used in the metallurgy of aluminum, occurs in Greenland, although the supply there has largely been mined out.

**377. Metallurgy of Aluminum.**—Up to the time of the revolutionary discovery of young Charles Martin Hall (1886), aluminum had been produced in a variety of ways from aluminum chloride.

Oersted (1825) and Wöhler (1827) reduced $AlCl_3$ with K; Deville (1855) lowered the price to $27 a pound by reducing $AlF_3$, $3NaF$ with Na; and the American chemist Castner (1880) brought the price down to $8 a pound by producing cheap electrolytic sodium (127). With a method similar to Castner's, Frismuth in Philadelphia (1884) cast the cap of the Washington monument, which as a lightning arrestor became the crown jewel for architectural aluminum.

In 1885 Charles Martin Hall, 22 years old and just graduated from Oberlin College, invented his important process for its manufacture. Heroult, in France, developed the same process almost simultaneously. Today, through the discovery of Hall, and through his tireless efforts in carrying the process through on the commercial scale, aluminum is 17 cents a pound, and annual production has increased from 85 pounds to far over half a million tons.

The Hall process consists in dissolving alumina, $Al_2O_3$ in molten cryolite, $AlF_3$, 3NaF, and electrolyzing. The operation is conducted in steel pots lined with carbon which constitutes the cathode (Fig. 131). Carbon blocks more than one foot square or large, solid carbon electrodes many feet in diameter are arranged to carry currents of 20,000 to 50,000 amperes, serving as anodes. They are immersed in the molten cryolite, which is kept molten by the heat produced by the passage of the current. More alumina is added during the process. The carbon anodes are consumed by the oxygen which is given off, a pound of carbon for each pound of aluminum; and as they burn away they must be repeatedly lowered into the molten bath and replaced. The aluminum is tapped and cast into pigs at intervals, without allowing the contents of the pot to "freeze." A flowsheet of the process, including several steps preliminary to the electrolysis, is given in Fig. 132.

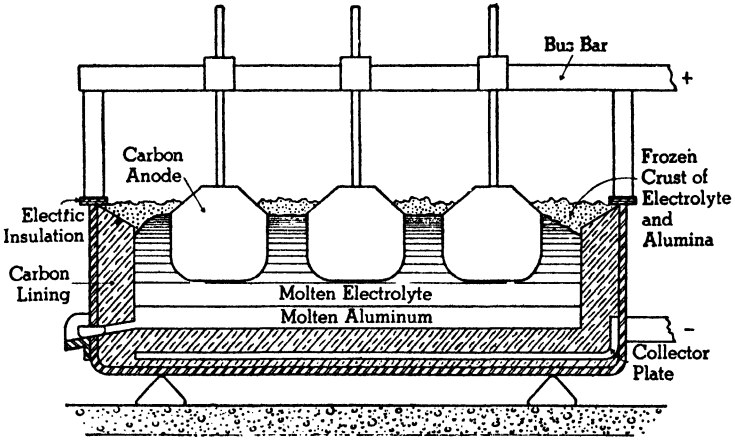
*Courtesy of the Aluminum Company of America*

FIG. 130. Charles Martin Hall, youthful discoverer of the electrolytic process for manufacturing aluminum.

In 1889 Hall organized a company for the commercial production of aluminum. It later became the Aluminum Company of America, which is the largest producer and fabricator of aluminum in the Western Hemisphere.

At the close of 1940, the company initiated a national defense program costing $200,000,000, which presaged a 1942 production of 360,000 tons of new aluminum, and a material increase in fabricating facilities. As a reflection

**upon some of their problems it is interesting to record that in 1940 they built a press for experiment and actual plant production which can apply pressures of 3,000,000 pounds per square inch, and yet is so sensitive that it could crush a watch crystal without stopping the watch.**



*Courtesy of the Aluminum Company of America*

FIG. 131. Hall's process for the manufacture of aluminum.

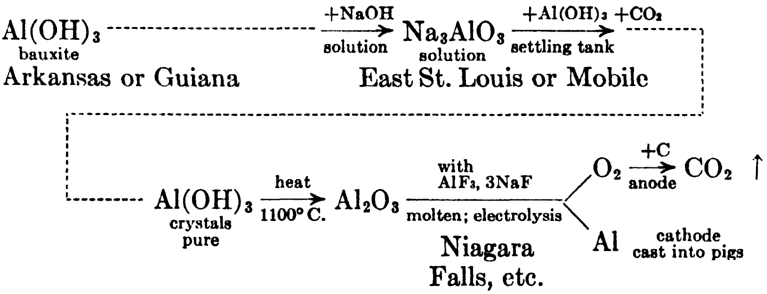


FIG. 132. The Bayer process as used by the Aluminum Company of America.

*Question*: write the equations for the processes represented above.

Impure aluminum is further **refined by the Hoopes process.** Carbon-lined tanks similar to those used in the Hall process contain three layers: (1) a heavy, molten alloy of copper, silicon and impure aluminum, the latter being replenished throughout the process; (2) a middle layer of fluorides of aluminum, sodium and barium nearly saturated with $Al_2O_3$; and (3) a top layer of pure aluminum. The electrodes are the reverse of the Hall process, *i.e.*, the bottom lining is the anode, and the top carbon rod is the cathode. When a current is passed, the aluminum passes from the impure bottom layer and gathers in the top layer as aluminum of purity up to 99.98 per cent.

**378. Properties.**— Aluminum is a silvery metal which resembles tin in appearance. It melts at 660° and boils at 1800°. The density of the pure metal is 2.7. Aluminum is the third most malleable and the sixth most ductile common metal, being especially malleable and ductile between 100°–150°. It is a good conductor of electricity, and although the tensile strength of the pure metal is rather low, the addition of alloying elements raises it to that of mild steel, or somewhat more. Because of its softness the pure metal requires special care in machining, but is easily polished. The alloys are more readily machined, and indeed some cast alloys machine better than cast iron, while certain wrought alloys machine as well as free-cutting brass. These alloys usually contain copper and in some cases also magnesium, manganese and zinc.

Aluminum combines readily with many non-metals, *e.g.*, the halogens, sulfur, oxygen, and so forth. The heat of formation of the oxide is very large, 133,000 calories per gram atom of oxygen.

This is to be compared with 100,900 cals. and 20,800 cals. per gram atom of oxygen in forming the oxides of sodium and iron. Only a few other oxides have heats of formation higher than that of aluminum oxide: $ThO_2$, 165,000 cals.; CaO, 152,000 cals.; $Nd_2O_3$, 145,000 cals.; MgO, 143,000 cals.; $Li_2O$, 142,000 cals.; SrO, 141,000 cals.; and BaO, 133,100 cals.

As a consequence of this high heat of formation of aluminum oxide, the following reaction is strongly exothermic:

$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe + 198{,}800 \text{ cals.}$$

### DEMONSTRATION 112. THERMIT AND OTHER REACTIONS

**Materials:** (*a*) Set-up as in Fig. 133; gloves, a second crucible of thermit mixture, long-handled spoon; (*b*) two aluminum photo-flash bulbs, one in socket connected to the current; (*c*) sheet of aluminum, mercury.

(*a*) Upon igniting the mixture the molten iron eats through the pan, under water. During the reaction additional thermit can be added. Alumina slag, $Al_2O_3$, can be separated from the molten iron. This is the principle involved in thermit welds and incendiary bombs. (*b*) When a photoflash bulb containing aluminum foil is ignited it becomes as hot as the surface of the sun (8000° A.); the heat and light are sufficiently great to ignite a second bulb held against it. A film of oxide is formed when the metal tarnishes in the air or in water, and prevents further action. (*c*) Mercury rubbed upon a sheet of aluminum forms an amalgam which disintegrates in moist air, forming white granules of aluminum hydroxide.

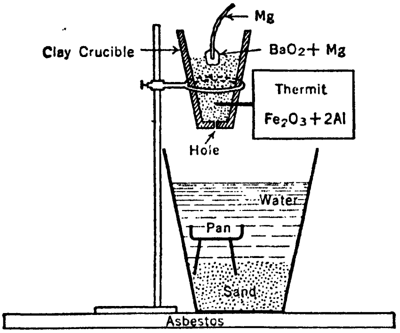


FIG. 133. The thermit reaction (Dem. 112).

Aluminum readily interacts with dilute hydrochloric acid and with hot solutions of hydroxides to form hydrogen (compare with zinc and tin):

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2,$$
$$2Al + 6NaOH \rightarrow \underset{\text{sodium aluminate}}{2Na_3AlO_3} + 3H_2.$$

Aluminum cooking utensils are not attacked by foods sufficiently to introduce harmful quantities of the metal.

**379. Uses of Aluminum.**—Since the metal is only one-third as heavy as iron, tarnishes but slightly, and its alloys are easily cast and welded, it is replacing steel in automotive and airplane parts.

Transportation on land and sea, and in the air, accounted for 29 per cent of the aluminum consumed in the United States between 1933 and 1938; 15 per cent was for machinery and electrical appliances; 14 per cent for cooking utensils; 10 per cent as electrical conductors; and the balance rather evenly distributed among the building, chemical, metallurgical, foundry, food and beverage industries. Aluminum is a better conductor of electricity than an equal weight of copper, and 10 per cent went for high-tension transmission wires, which usually have a high-tensile-strength steel core. The remainder of the aluminum consumption was in cooking utensils (14 per cent), as substitute for tin in foil and toothpaste tubes, for degassing molten steel, and in metal working. Aluminum powder suspended in oil forms a paint possessing great covering power. In Germany and other countries where tin is scarce and aluminum accessible, the latter is being abundantly substituted.

Aluminum sheet is rolled from large cast ingots, the first operation being hot rolling at temperatures between 400 and 500° C. The resulting "slab," which may be between ¼" to ½" thick, is then cold rolled to the required thickness, with or without intermediate annealing, as may be required to produce the desired temper and thickness. Cooking utensils or other similar articles would be drawn or spun from such sheets, and in many cases, such as tea-kettles, tanks, etc., the parts drawn or otherwise formed would be united by welding and finished by grinding and perhaps polishing.

Early **alloys of aluminum** were not especially promising. But in 1906 Wilm patented an alloy, **duralumin,** possessing remarkable properties. Duralumin contains about 4 per cent Cu, 0.6 per cent Mg, 0.6 per cent Mn, and the remainder aluminum, and is essentially a solid solution of $CuAl_2$ and $Mg_2Al$. Wilm discovered that, like steel, the properties of this alloy could be improved by heat treatment. The resulting alloy had substantially the strength and elongation of mild steel, and was therefore suitable for structural uses such as in airplanes, dirigibles, truck bodies, railroad cars, etc. Subsequent small changes in composition, and improvement in technique, which permit the working of stronger and harder alloys, have recently produced a product which is decidedly superior to the original duralumin in its properties.

A decided improvement in the behavior of the thin sheets of duralumin-type alloy in airplanes was made when the Aluminum Company of America developed the composit "Alclad" sheet, in which a strong alloy core of the duralumin type is covered on each side with about 5% of its thickness of pure aluminum. The resulting sheet is remarkably resistant to corrosion.

The **thermit process** has already been described in some detail (**378**). The thermit-weld is used for repairing cracked propellors, steel rails, etc., which can be fixed *in situ.* War-time incendiary bombs of thermit contain a mixture of iron oxide and powdered aluminum or magnesium; even the case of the bomb is made of an alloy which will burn. The mixture reaches a temperature of 3000° C., and white-hot iron runs out upon the bombed object.

## COMPOUNDS OF ALUMINUM

**380. Oxide and Hydroxide of Aluminum.**—**Aluminum oxide** or **alumina,** $Al_2O_3$, occurs in nature as a *corundum,* of which the precious stones *ruby* and *sapphire* are varieties. White sapphires are pure oxide; ruby red is due to traces of chromium; and sapphire is blue, due to traces of titanium or iron. Emery is a compact form of corundum containing large quantities of iron oxides.

In the manufacture of **gems** the pulverized oxides are melted in the oxy-hydrogen flame. The droplets are caught on a disc in the flame and built up in the shape of an inverted chestnut.

**Alumina** is made on a large scale by calcining the purified $Al(OH)_3$ extracted from bauxite (section **377**); a white substance of the same crystalline structure as the natural mineral corundum, practically insoluble in water and melting at 2050° C., is obtained. It is used for abrasives and laboratory ware (*e.g., Alundum, Crystallon, etc.*).

**Aluminum hydroxide,** $Al(OH)_3$, may be easily obtained in the laboratory by treating a solution of an aluminum salt with ammonium hydroxide. Although when produced commercially from bauxite (section **377**) it is a white, sandy (crystalline) material, the laboratory product is a white, gelatinous precipitate, which upon drying is shown by X-ray diffraction to be a mixture of the crystalline hydrates $Al(OH)_3$ and $Al(O)OH$. It is insoluble in water, amphoteric in character; (*a*) with acids it gives a salt and water, and (*b*) with metallic hydroxides it also gives a salt and water.

$$Al^{+++} + 3OH^- \rightleftarrows Al(OH)_3 \begin{cases} \rightleftarrows 3H^+ + \underset{\text{aluminate}}{(AlO_3)^{\equiv}} \\ \rightleftarrows H_2O + H^+ + \underset{\text{meta-aluminate}}{(AlO_2)^-} \end{cases}$$

$$(a) \qquad Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$$

$$(b) \qquad H_3AlO_3 + 3NaOH \rightarrow \underset{\substack{\text{sodium}\\\text{aluminate}}}{Na_3AlO_3} + 3H_2O$$

### DEMONSTRATION 113. ABSORPTIVE POWERS OF $Al(OH)_3$

Materials: Five cylinders of water, solutions of alum, $NH_4OH$, alizarin, mud, indigo, *aluminon.*

When $Al(OH)_3$ is formed in the presence of dyes or mud, by mixing $NH_4OH$ and alum, it settles as a gelatinous precipitate, carrying the dyes and mud with it. This property is used in mordanting (**643**) in which the $Al(OH)_3$ is precipitated in the textile fibres and holds the dye to the cloth; and in clarifying muddy waters.

**381. The Alums.**—Some important **alums** are

| | |
|---|---|
| Potash (common) alum | $K_2SO_4$, $Al_2(SO_4)_3$, $24H_2O$ |
| Sodium alum | $Na_2SO_4$, $Al_2(SO_4)_3$, $24H_2O$ |
| Ammonium alum | $(NH_4)_2SO_4$, $Al_2(SO_4)_3$, $24H_2O$ |
| Chrome alum | $K_2SO_4$, $Cr_2(SO_4)_3$, $24H_2O$ |
| Ferric alum | $(NH_4)_2SO_4$, $Fe_2(SO_4)_3$, $24H_2O$ |

In agreement with these formulas, an alum is a double salt (which may or may not contain aluminum) of the general formula

$$M_2{}^{+}SO_4,\ M_2{}^{+++}(SO_4)_3,\ 24H_2O$$

$M^+ = Na^+, K^+, Rb^+, Cs^+, NH_4{}^+$, or $Ag^+$; $M^{+++} = Al^{+++}, Cr^{+++}$ or $Fe^{+++}$.

They are formed by mixing sulfates of univalent metals with sulfates of trivalent metals, and allowing crystallization to take place: *e.g.*, potash alum, $K_2SO_4$, $Al_2(SO_4)_3$, $24H_2O$, can be prepared by dissolving potassium sulfate and aluminum sulfate in equimolecular proportions and allowing the water to evaporate. The transparent crystals are octahedral and belong to the regular or isometric system. The simpler formula $M^+M^{+++}(SO_4)_2$, $12H_2O$ is often used for the alums.

**Aluminum sulfate,** $Al_2(SO_4)_3$, $18H_2O$ has largely replaced the alums in industry since it is cheaper, containing a higher weight-per cent of aluminum.

Production in the United States in 1939 was as follows: ammonium and potassium alums 7649, sodium alum 31,545, and aluminum sulfate 438,692 short tons. Of this latter, 10,278 tons was used for purifying municipal water supplies; the remainder was used in the manufacture of paper, as a mordant, in baking powder, and in certain foods (*e.g.*, pickles). The sulfate is prepared by roasting bauxite or clay (kaolin), to form insoluble iron oxides, and then dissolving out the alumina in sulfuric acid.

**382. Aluminum Silicates.**—Igneous rocks make up a large part of the solid shell of the earth. These rocks contain on the average nearly 60 per cent of the **feldspars** $KAlSi_3O_8$ and $NaAlSi_3O_8$. The potash feldspars are called orthoclase and microcline, and the soda feldspar, albite. By the weathering of feldspars, which is partly chemical and partly mechanical, aluminum silicate, or clay, is formed (474); also, other components of the soil. The mineral **kaolinite,** $Al_2H_2(SiO_4)_2$, $H_2O$, is a pure variety of clay which is sometimes found deposited extensively in beds. More frequently, however, the kaolinite is carried away by running water and deposited along with other substances such as sand and compounds of iron, calcium, and magnesium, forming what is known as common clay.

**Kaolin** is a pure form of clay, which burns white when heated, forming the basis of fine pottery and porcelain. The impure varieties of clay are utilized in the manufacture of tile, drain-pipes, bricks, etc. **Fuller's earth** is a variety of absorbent clay. It is variegated in color, and is employed on a large scale for removing the color from mineral oils. **Bentonite** is a colloidal clay which swells in water. It is used as a filler in rubber, a dispersing agent in emulsions, and a bonding clay in lead pencils.

**383. Ceramics.**—Finely-divided wet clay will absorb water to form a plastic mass. Upon heating this, the water is expelled and pottery, porcelain, brick, tile and so forth are produced. **Ceramics is the art of producing these materials, and the study of their properties.**

**Prehistoric pottery** was made often by kneading wet clay upon stone slabs, fashioning into the desired object, and baking in the sun. Such pottery was soft and porous, like mud-wasp nests, but suitable for holding grain and the like. When fire is substituted for the sun, the clay is dehydrated, and the metallic oxides which remain turn various hues: red, brown, buff, and drab (Fig. 134).

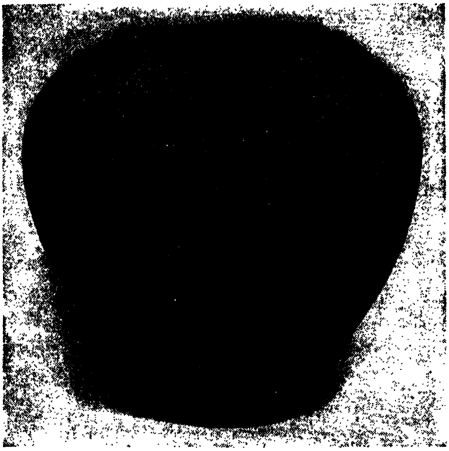


FIG. 134. Egyptian jar of the predynastic period.

**Modern pottery** is made as follows. Finely divided clay is suspended in water (**slip**) until needed. Some of the water is expressed and the clay is kneaded in a pugging machine and worked up into a plastic mass. This mass is then formed into the desired shape on a potter's wheel (which was used even in Biblical times: Jer. 18:3), or in a spinning mold, or in a casting mold. The shaped clay is placed in fire-clay pots (saggers) stacked in a **kiln,** and heated to about 1400°, where the water is expelled and other changes occur. The product of this **first firing** is a porous material called **bisque.** To make it water-tight, the bisque is coated with a paste of silicates (sand, feldspars) and **fired a second time.** The final glaze is obtained by a **third firing,** before which metallic oxides are added to form colored silicate enamels (*e.g.*, cobalt blue, chromium green, *etc.*)

Other ceramic products are **hard porcelain,** obtained by firing a high-silica clay above 1600°; **porous ware** (bricks, terra-cotta, common crockery) which are low-temperature fired, usually containing red oxide of iron ($Fe_2O_3$), and may be glazed by throwing NaCl into the kiln (what forms?); and **refractories,** or **fire-bricks** which contain oxides of magnesium, chromium, etc., to withstand high temperatures. Magnesite, $MgCO_3$, was once the chief source of this magnesia; but today dolomites (338) are equally important; and about a million metric tons of each are annually used in lining open-hearth and blast furnaces.

**384. Analysis of Aluminum.** $NH_4OH$ or $(NH_4)_2S$ precipitates aluminum as white gelatinous aluminum hydroxide, which is insoluble in the presence of ammonium salts. Sodium or potassium hydroxide produces the same precipitate, which dissolves in excess of the reagent. When an aluminum compound is moistened with cobalt nitrate and then heated strongly, blue cobalt meta-aluminate, $Co(AlO_2)_2$, is formed.

Also, aluminum hydroxide absorbs certain dyes (forms lakes), in particular with an analytical reagent trade-marked **aluminon** (a complex organic compound, ammonium aurin tricarboxylate) it forms a red flocculate.

**385.—**

TABLE 78. USES FOR GROUP III COMPOUNDS

| | |
|---|---|
| **Rare Earths** | **rare earths, cerium, ceria, monazite sand, silicates, ceric sulfate** (373). |
| **Group III-A** | **yttrium, scandium, actinium** (374). |
| **Group III-B** | **gallium, indium, thallium, thallous nitrate** (375). |
| Thallium sulfate $Tl_2SO_4$ | rat poison, insecticide. |
| **Aluminum and its compounds** | **Al(376-9), Duralumin, Alclad (379); $Al_2O_3$ and hydroxide (380), alums, sulfate (381), silicates (382).** |
| Aluminum acetate $Al(CH_3COO)_3$ | strongly hydrolyzed to $Al(OH)(CH_3COO)_2$; mordant; preparing lakes (380); waterproofing fabrics; embalming. |
| Aluminum chloride $AlCl_3$ | white crystals which fume in air from hydrolysis; catalyst for organic reactions; refining mineral oils, petroleum polymerization and cracking catalyst; 11,000 tons produced in the U. S. A. in 1939. |

## QUESTION REVIEW

I. GROUP III-A. The rare earth metals (373). Other members (374).

1. Show why, on the basis of electronic structure, there are 15 rare earth metals.
2. Discuss the rare earth metals as regards (*a*) chemical behavior, (*b*) relative abundance of the elements with odd and with even atomic numbers.

II. THE ALUMINUM FAMILY.

**a. Characteristics of Group III-B (375).**

3. Compare and contrast the properties of members of this group.

III. ALUMINUM.

**a. History and occurrence (376). Metallurgy (377).**

4. Give equations showing (*a*) the weathering of feldspar, (*b*) preparing bauxite for the Hall process, (*c*) the Hall process.
5. What countries furnish bauxite to the top three aluminum producers of the world?
6. Why would a strike in the aluminum-producing industry be more serious than a corresponding strike in, let us say, the garment industry?
7. How is aluminum refined?

**b. Properties (378). Uses (379).**

8. What properties of aluminum suit it for its various industrial applications?
9. Show by equations what occurs when aluminum chloride is treated with increasing amounts of sodium hydroxide.
10. Give two equations showing aluminum compounds hydrolyzing.
11. What discovery revolutionized the aluminum-alloy industry? What new product has appeared?
12. Give an equation and discuss thermit.

**c. Compounds of aluminum.**

**(1) Aluminum oxide and hydroxide (380).**

13. Name some naturally occurring oxides and hydroxides of aluminum. Show by equations that the latter is amphoteric.
14. To what use is this amphoteric property put in the metallurgy of aluminum?

(2) **Alums (381).**

15. Give the formulas for (*a*) potash alum, (*b*) chrome alum, (*c*) the cheapest aluminum salt. Approximately how much of each is produced annually?

(3) **Aluminum silicates (382). Ceramics (383).**

16. What is kaolin used for? Fuller's earth? Bentonite?
17. How is each of the following made: glazed brick, firebrick, terra-cotta, a porcelain bowl, pottery similar to prehistoric pottery? Why is the refractory industry a key industry?

**d. Analysis of aluminum (384).**

18. Why does not $Al_2S_3$ precipitate when $(NH_4)_2S$ is added to a solution containing $Al^{+++}$?
19. Explain how the absorptive properties of aluminum hydroxide are utilized in the (*a*) dye industry, (*b*) analytical analysis for aluminum, (*c*) purifying water.

IV. **Uses for Group III compounds (385).**

20. Name 5 compounds of the elements in group III, and give an important industrial use for each.

**Reading References:** Articles in the Appendix:

*Aluminum:* 23, 28, 123, 200, 202, 222, 235, 301, 302 and 338.

*General:* 61. 140, 218 and 238.

# CHAPTER XXIX

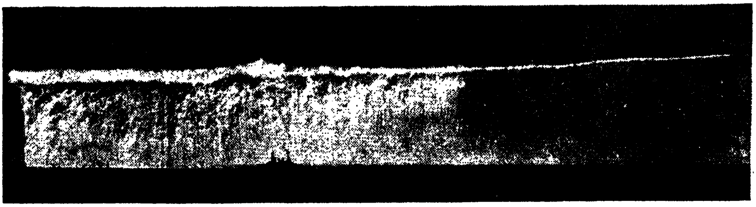
## GROUP IV-A AND THE TIN GROUP

**386. Group IV-A.**—The members of group IV-A are metals; and as would be anticipated, the metallic properties increase as we go down in the column. Thus titanium is so inactive a metal that its chloride hydrolyzes in air.

DEMONSTRATION 114. SMOKE SCREEN

Materials: Two 4 ft. lengths of Bunsen-burner tubing, 4 ft. length of 6 mm. glass tubing, 200-cc. washing-bottle, $TiCl_4$, concentrated HCl, $NH_4OH$.

If air is blown through 2 cc. of $TiCl_4$ it is hydrolyzed by the moisture in the air, and smoke is given off; when conducted through the glass tubing, "sky-writing" may be performed (Fig. 135). If this compound is used in airplanes, ammonia is also ejected from the plane to react with the HCl and form additional smoke:



*Courtesy, C.W.S., War Department*

FIG. 135. Smoke screen laid down by an airplane off Cape Hatteras, N. C.. An example of hydrolysis.

$$TiCl_4 + 4H_2O \rightarrow 4HCl + Ti(OH)_4 \rightarrow \underset{\text{white clouds}}{TiO_2} + 2H_2O,$$

$$HCl + NH_4OH \rightarrow H_2O + \underset{\text{white clouds}}{NH_4Cl}.$$

Both titanium and zirconium hydroxides are amphoteric, but the lower three members of the family are distinctly metallic in their properties.

TABLE 79. GROUP IV-A

| Element | Atomic Weight | Atomic Number | Arrangement of Planetary Electrons | Density | M.P. | B.P. |
|---|---|---|---|---|---|---|
| Titanium, Ti | 47.9 | 22 | 2-8-(8+2)-2 | 4.5 | 1800° | >3000° |
| Zirconium, Zr | 91.22 | 40 | 2-8-18-(8+2)-2 | 6.4 | 1700° | >2900° |
| Cerium, Ce | 140.13 | 58 | 2-8-18-(18+1)-(8+1)-2 | 6.9 | 640° | 1400° |
| Hafnium, Hf | 178.6 | 72 | 2-8-18-32-(8+1)-2 | 13.3 | 2207° | >3200° |
| Thorium, Th | 232.12 | 90 | 2-8-18-32-18-(8+1)-2 | 11.2 | 1845° | >3000° |

**Titanium** occurs as rutile, $TiO_2$, and ilmenite, $FeTiO_3$. The former is mined in many localities, especially Virginia and Arkansas, and is used in ceramics and for welding-rod coatings. Ilmenite has enjoyed a spectacular rise to importance during the past fifteen years. First used as a paint pigment in 1919, there were 5000 tons imported in 1926, and 286,576 tons in 1939. It comes from India. The pigment, titanium white, improves the whiteness, covering power and weathering characteristics of paints. Recently Kennametal, an ultra-hard cutting-tool alloy of titanium-tungsten, was announced.

**Zirconium** occurs in zircon, $ZrSiO_4$, and also is associated with rutile. Its importance is chiefly in the ceramic industry, special porcelains for electrical appliances, tough glass, a refractory for crucibles, (provided iron oxides are not being used), and as an opacifier in vitreous enamels, a use in which it has now replaced tin oxide.

**Hafnium** was discovered in 1923 by Costa and Hevesy, of Copenhagen (Latin *hafniae*). None is produced in the United States.

**Cerium** and **Thorium** occur in monazite sand (373). With the demise of the Welsbach gas mantel (99 per cent $ThO_2$) monazite production fell from 7392 tons in 1909 to less than 100 tons by 1930; but it unexpectedly increased to over 6000 tons by 1938. Half came from India, 10 per cent from Brazil, and none from the United States. The increase of **cerium salts** for mothproofing fabrics, for coloring topaz-yellow glass, for opacifying enamels and for stabilizing the arcs of carbon lamps may account for the increased consumption. An alloy containing 80 per cent Ce and 30 per cent Fe is used for so-called "flint" lighters: when small particles of the alloy are struck off, they ignite spontaneously.

Cerium is a rare earth metal but it is also included in Group IV-A because it forms a series of important **ceric compounds**, which are used as oxidizing agents in analysis. For example, the volume of a 1 N ceric sulfate solution necessary to oxidize completely a ferrous sulfate solution of unknown strength will determine the concentration of the latter solution.

$$2FeSO_4 + \underset{\text{reddish}}{2Ce(SO_4)_2} \rightarrow Fe_2(SO_4)_3 + \underset{\text{pale yellow}}{Ce_2(SO_4)_3}.$$

**Thorium** has no important use, at present. It is radioactive (251).

### THE TIN GROUP: Ge, Sn, Pb.

**387. Characteristics of Group IV-B.**—The metals of the Tin Family are **germanium, tin** (*stannum*), and **lead** (*plumbum*). These elements constitute Group IV of the Periodic System, and are related to the non-metals, carbon and silicon.

We may regard the elements of Group IV as a transition group, linking the more metallic elements of Groups I to III with the more non-metallic elements of Groups V to VII. This means that metals predominate in Groups I to III and non-metals in Groups V to VII, whereas in Group IV there is a sort of balance between metals and non-metals. In accordance with the general rule, the metallic character increases with increase in atomic weight, lead being the most metallic element of Sub-group B.

The metals of the tin group are silvery white, easily fusible, and are not readily affected when exposed to the air. The metals of the titanium group are difficultly fusible.

The metals of the tin group unite directly with chlorine to form dichlorides and tetrachlorides—$MCl_2$ and $MCl_4$.

Tin and lead are not known to form hydrides, but they form *organo-metallic compounds*, such as lead tetraethyl, $Pb(C_2H_5)_4$.

Some of the properties of the members of the tin group are summarized in the table below.

TABLE 80. THE TIN GROUP

| Element | Atomic Weight | Atomic Number | Arrangement of Planetary Electrons | Density | Melting Point | Boiling Point |
|---|---|---|---|---|---|---|
| Germanium, Ge | 72.6 | 32 | 2–8–18–4 | 5.36 | 958° | 2700° |
| Tin, Sn | 118.7 | 50 | 2–8–18–18–4 | 7.31 | 232° | 2270° |
| Lead, Pb | 207.22 | 82 | 2–8–18–32–18–4 | 11.35 | 327.5° | 1620° |

**388. Germanium.**—Predicted by Mendeléeff in 1869, this element was discovered by Winkler 17 years later in a Freiberg silver ore (Latin, *germania*). It occurs in some quantities in zinc blende, but is of no use. The metal may be prepared by reducing germanium dioxide, $GeO_2$, with carbon at a high temperature. Germanium melts at 958°, boils at 2,700°, and has a density of 5.36. It resembles silicon, but is more metallic in its physical properties.

## TIN $^{118.7}_{50}Sn$

**389. History and Occurrence.**—Tin has been found in Egyptian tombs; and the Cassiderides, "Tin Islands," deposits of Cornwall supplied the ancient world. E. R. Caley (1938) has shown that tin in coins was abruptly replaced by lead after the fall of Carthage put an end to the tin trade; one can therefore date certain ancient bronze coins by their tin-lead content. Bronze, an alloy of copper and tin, was also very common in ancient times.

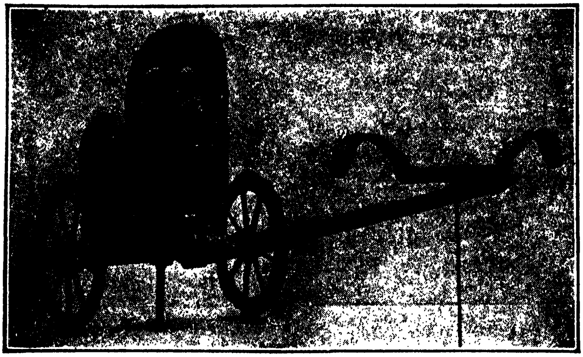


FIG. 136. Etruscan metalwork. Bronze chariot, sixth century B.C.

The chief ore is **cassiterite** or **tinstone, $SnO_2$.**

An International Tin Control regulated 85 per cent of the world's 181,000-ton 1939 production. The Malay States (30 per cent of world total), the Dutch East Indies (17 per cent), Bolivia (15 per cent), and six less important producers are signatories of this Control Scheme. The United States is lacking in this strategic material, the largest domestic deposit being an estimated 148,000 tons in the Black Hills of South Dakota.

**390. Metallurgy.**—The metallurgy of tin is carried out as follows:

(*a*) The tinstone is crushed and the lighter earthy matter washed away. The gravity method of concentration is also employed, and the heavy tin ore settles.

(*b*) The ore is next roasted, if necessary, to remove arsenic, antimony, and sulfur.

(*c*) The ore is then reduced with coal or charcoal in a reverberatory or blast furnace:

$$SnO_2 + 2C \rightarrow Sn + 2CO.$$

(*d*) The metal is purified by remelting. When the cast slabs of tin are melted on the sloping hearth of a reverberatory furnace, the molten tin runs into a basin, while the iron remains behind.

In 1938 there was 21,000 tons of tin recovered by treating old "tin cans" and scrap tin-plate with chlorine. Stannic chloride, $SnCl_4$, is formed, which is used in dyeing.

**391. Properties.**—Tin is a silvery white metal, melting at 232° and boiling at 2,260°; its density is 7.31, and it is a soft metal of no great tensile strength. When cold, it is rather brittle; and when a bar of the metal is bent, a crackling sound is emitted, known as the "tin cry." Tin is malleable at about 100°, and at that temperature it may be rolled into tin foil and drawn into pipes.

There are two allotropic forms of tin: **gray tin** and **white (tetragonal) tin.** Gray tin has a density of 5.75.

$$\text{gray tin} \overset{>13^\circ}{\rightleftarrows} \text{white tin}$$

The transformation of the common white tin into the gray modification is known as the "tin pest." During the cold winter of 1867–8 the tin pipes of an organ in Leningrad crumbled to a gray powder (Fig. 137).

Tin forms stannous compounds with dilute or concentrated HCl, or dilute $HNO_3$. Tin forms stannic compounds with hot concentrated sulfuric acid, and with concentrated nitric acid; although in the latter case the stannic nitrate hydrolyzes further to metastannic acid ($SnO, 2H_2O$, or $H_2Sn_5O_{11}, 9H_2O$, formula variable). The metal combines with alkali hydroxides to form stannites.

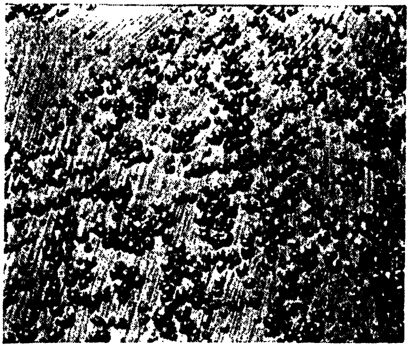


FIG. 137. Tin pest. White tin at low temperatures slowly changes to the grey modification.

$$\begin{aligned}
Sn + 2HCl &\rightarrow SnCl_2 + H_2 \uparrow \\
Sn + 4H_2SO_4 &\rightarrow Sn(SO_4)_2 + 2SO_2 + 4H_2O \\
4Sn + 10HNO_3 &\rightarrow 4Sn(NO_3)_2 + 3H_2O + NH_4NO_3 \\
Sn + 2NaOH &\rightarrow Na_2SnO_2 + H_2 \uparrow
\end{aligned}$$

**392. Uses.**—Tin is used principally in the manufacture of tin plate, a use which depends upon the fact that tin does not tarnish when exposed to moist air or to the organic acids in food.

**Tin-plate** is manufactured by dipping cleaned sheets of low-carbon steel into molten tin. The iron is thoroughly protected from corrosion so long as the coat of tin remains intact; but if the layer of tin be damaged, thus exposing the iron, corrosion of the latter is actually hastened, the tin serving as a contact agent. Ordinary **pins** are produced from brass wire and then coated with tin by treatment with a solution of a tin salt. Some of the zinc of the brass displaces tin, which coats the pins.

Consumption of tin during 1939 in the United States included tin-plate, 40 per cent; solder, 22 per cent; babbitt low-melting alloy, 7 per cent; bronze, 7 per cent; and collapsible tubes and foil, 2 per cent.

**393. Stannous Hydroxide.** The **hydroxide** is amphoteric, as is shown by treating stannous chloride with successive portions of an alkali:

$$\underset{\substack{\text{stannous}\\\text{chloride}}}{SnCl_2} \xrightarrow{KOH} \underset{\substack{\text{(white)}\\\text{stannous}\\\text{hydroxide}}}{Sn(OH)_2} \xrightarrow{KOH} \underset{\substack{\text{potassium}\\\text{stannite}}}{K_2SnO_2}.$$

**394. Stannic oxide and Metastannic Acid.**—Cassiterite, $SnO_2$, occurs in nature. It may be obtained as a white powder by heating tin in air; also when metastannic acid (**394**) is ignited. Stannic oxide is insoluble in water and acids (*i.e.*, when strongly ignited).

**Metastannic acid,** $H_2SnO_3$, sometimes called *α-stannic acid* or simply *stannic acid*, is hydrated $SnO_2$ (*i.e.*, $SnO_2$, $H_2O$). It is formed as a white gelatinous precipitate by the following reaction:

$$SnCl_4 + 4NH_4OH \rightarrow 4NH_4Cl + \underset{\substack{\text{metastannic}\\\text{acid}}}{H_2SnO_3} + H_2O.$$

When metastannic acid is heated it loses water, forming $SnO_2$.

The corresponding sodium salt, **sodium metastannate,** $Na_2SnO_3$, $3H_2O$ is used as a mordant and for fireproofing cotton goods.

The fabric is fireproofed by first soaking it in a solution of a metastannate; it is then dried, and treated with a solution of ammonium sulfate. The ammonium stannate undergoes hydrolysis, and the stannic acid which is formed cannot be washed out. When the fabrics are dried, the acid has a tendency to lose water to form stannic oxide.

**395. Stannic chloride.**—$SnCl_4$ is prepared by heating tin with an excess of chlorine. It is a heavy, colorless, fuming liquid, boiling at 114.1°. In conjunction with small quantities of water it forms crystalline hydrates, such as $SnCl_4$, $5H_2O$. This hydrate is used as a mordant. When treated with water the hydrates dissolve and in dilute solutions completely hydrolyze to form a colloidal suspension:

$$SnCl_4 + 4HOH \rightarrow \underset{\text{colloidal}}{Sn(OH)_4} + 4HCl.$$

### LEAD $^{207.2}_{82}Pb$

**396. History and Occurrence.**—Lead was one of the seven metals known to the ancients.

Articles manufactured of lead have been found in Egyptian tombs of great antiquity, and the metal is mentioned several times in the writings of the Old Testament. The ancient Romans utilized lead for water pipes, and certain lead compounds were used as paint and cosmetics. The Romans called it *plumbum*; hence the symbol Pb.

Lead occurs chiefly as the mineral **galena** or **galenite,** PbS, which crystallizes in the isometric system. Galena contains as impurities zinc, copper, cadmium, arsenic, antimony, and bismuth, perhaps as sulfides; also silver and gold. The silver value of galena is often greater than that of the lead. **Cerussite,** $PbCO_3$, and **anglesite,** $PbSO_4$ are also important ores of lead. The lead producers of the world are shown in Table 81.

TABLE 81. LEAD PRODUCERS

| World Producers (metric tons, 1939) | | United States (metric tons, 1939) | |
|---|---|---|---|
| United States (refined) | 404,257 | Missouri | 156,281 |
| Australia | 252,383 | Idaho | 90,981 |
| Mexico | 219,300 | Utah | 67,634 |
| Germany | 181,440 | All others | 99,083 |
| All others | 642,620 | | |
| **Total** | **1,700,000** | **Total (mined)** | **413,979** |

The lead produced in the Mississippi Valley is mostly "soft lead," for the ores from which it is produced contain but little silver. "Desilverized lead" amounts to over two-thirds of our annual production.

**397. Metallurgy of Lead.**—

**a. Concentration.** The ore, which usually contains from 5 to 10 per cent of lead, is crushed and concentrated by flotation; selective flotation methods (**290**) are used to separate galena (PbS) from zinc blende (ZnS) and other sulfides.

**b. Smelting.** The smelting of lead ores is usually carried out in blast furnaces. The ore or concentrate is first roasted in order to convert sulfide to oxide and sulfate, and the product is then charged into blast furnaces with suitable fluxes and coke. A strong blast of air is passed through the charge, and the lead oxide is reduced, largely by the carbon and carbon monoxide:

$$\begin{aligned} 2PbS + 3O_2 &\rightarrow 2PbO + 2SO_2, \\ 2PbO + C &\rightarrow 2Pb + CO_2, \\ PbO + CO &\rightarrow Pb + CO_2. \end{aligned}$$

The iron oxide formed is reduced by carbon monoxide to iron, which interacts with lead sulfide to form more lead:

$$PbS + Fe \rightarrow Pb + FeS.$$

Other reactions undoubtedly occur; involving for example, PbS, PbO, and $PbSO_4$ formed from the oxidation of PbS:

$$\begin{aligned} PbS + PbSO_4 &\rightarrow 2Pb + 2SO_2. \\ PbS + 2PbO &\rightarrow 3Pb + SO_2. \end{aligned}$$

If limestone is used as a flux, it combines with silica to form an infusible slag, calcium silicate:

$$CaO + SiO_2 \rightarrow CaSiO_3.$$

The impure lead settles to the bottom of the crucible, whence it is drawn off into molds.

**c. Refining.** Approximately two-thirds of our domestic lead ores do not contain any silver. In this event they are refined by slowly melting the lead in a jet of steam, which oxidizes iron, arsenic, antimony and tin impurities to form a scum.

In case lead ores contain valuable quantities of the precious metals silver and gold, the metal is usually obtained by the Parke process (325).

A third refining method is the **Betts** electrolytic process. Slabs of crude lead anodes and pure sheet-lead cathodes are immersed in a bath of lead fluosilicate, $PbF_2$, $SiF_4$. Pure lead deposits out on the cathode; iron passes into solution; and copper, antimony, bismuth and silver drop as anode mud or remain on the anode skeleton.

**398. Properties and Uses of Lead.**—Lead is a silver-white metal, with a density of 11.4; it melts at 327° and boils at about 1,620°. The metal is soft and malleable, and while warm it may be fashioned into pipes by means of hydraulic pressure.

Chemically, lead is not very active, its position being below tin and above hydrogen in the electromotive series. Lead oxidizes only superficially in the air, a final covering of basic carbonate being formed, which protects the metal beneath. When hard water remains in contact with lead pipes, a coating of the sulfate or the carbonate is formed, which protects the metal from further attack by the water. Soft water interacts with lead, however, to form the hydroxide, $Pb(OH)_2$, which is appreciably soluble, and the lead-ion ($Pb^{++}$) is highly poisonous. When heated in air, it forms PbO or $Pb_3O_4$, the latter being formed at lower temperatures. Most acids, excepting hydrochloric and sulfuric acids, interact with lead to form salts. Thus, it dissolves in nitric acid to form lead nitrate, and in acetic acid, forming lead acetate. Hydrochloric and sulfuric acids attack lead but slightly, for the chloride and sulfate are sparingly soluble.

Of the 667,000 short tons of lead consumed in the United States in 1939 thirty per cent, 200,000 tons, went for storage batteries; this is a source which returns quickly to the trade as scrap. White lead and cable-covering each consumed about 75,000 tons; lead oxides, building, and ammunition accounted for approximately 50,000 tons each; and solder, terneplate, and calking used about 20,000 tons apiece.

Antimony is one of the chief alloying elements used with lead. The lead of the storage battery is so alloyed; for without it the lead would be too soft. Lead for shot is hardened either with a little arsenic or antimony. The addition of the foreign metal renders the lead more fluid in the liquid state, increases the tendency to assume the spherical form, and makes the shot harder. Shot is manufactured by allowing the molten metal to fall from a tower, through openings in colanders, into water.

**399. Oxides and Hydroxides.**—

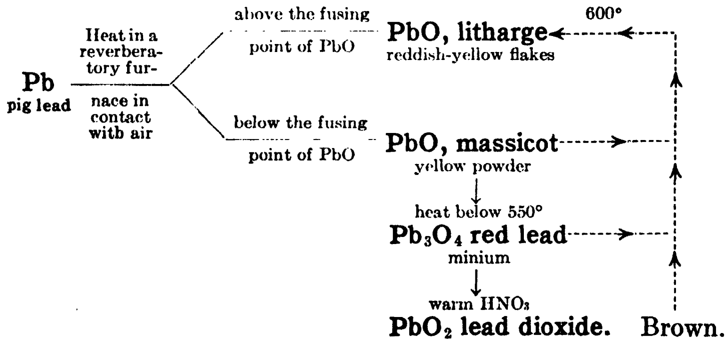

Pb
pig lead
Heat in a reverberatory furnace in contact with air
above the fusing point of PbO
below the fusing point of PbO
PbO, litharge
reddish-yellow flakes
600°
PbO, massicot
yellow powder
heat below 550°
Pb₃O₄ red lead
minium
warm HNO₃
PbO₂ lead dioxide. Brown.

FIG. 138. Oxides of lead.

All of the oxides of lead revert to PbO when heated in air above 600°. **Litharge** is used extensively in the manufacture of flint glass, as a glaze for pottery, and for preparing compounds of lead. Mixed with glycerine it sets to a hard cement useful in research work. **Red lead, or minium,** is used in flint glass and as the orange-colored pigment usually seen as the first coat on steel-girder construction. It is really not an oxide, but *lead orthoplumbate*, $Pb_2PbO_4$, inasmuch as $PbO_2$ is obtained when $Pb_3O_4$ is warmed with dilute $HNO_3$, *i.e.*:

$$Pb_2PbO_4 \xrightarrow{4HNO_3\text{ dil.}} H_4PbO_4 \xrightarrow{\text{warm}} PbO_2.$$

Other orthoplumbates with the formula $M_4PbO_4$ are known. **Lead dioxide,** $PbO_2$, is a powerful oxidizing agent used in organic syntheses, and as a brown paste in storage batteries.

DEMONSTRATION 115. AMPHOTERIC LEAD HYDROXIDE

**Materials:** Three test glasses, solutions of $Pb(NO_3)_2$ and KOH.

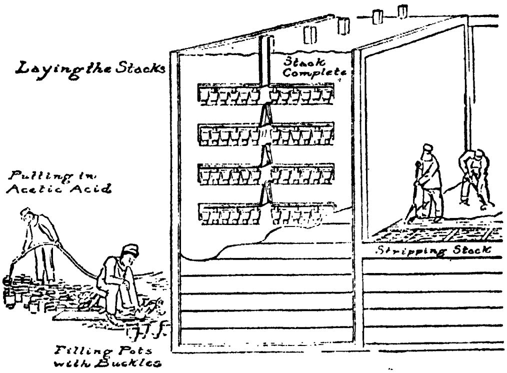
**Lead hydroxide,** $Pb(OH)_2$, like the corresponding hydroxides of other weak metals (*e.g.*, Zn, Al, Sn), is amphoteric:

$$\underset{\text{lead nitrate}}{Pb(NO_3)_2} \xrightarrow{\text{KOH}} \underset{\substack{\text{lead hydroxide}\\\text{(white)}}}{Pb(OH)_2 \downarrow} \xrightarrow{\text{KOH excess}} \underset{\substack{\text{potassium}\\\text{plumbite}}}{K_2PbO_2}.$$

**400. White Lead.**—Lead carbonate, $PbCO_3$ occurs in nature as cerussite. When alkali carbonates are added to lead salts an insoluble salt is formed, often called **basic lead carbonate,** or **white lead,**

$$\mathbf{Pb(OH)_2,\ 2PbCO_3.}$$

**The Dutch process** for producing white lead has been in operation for over 300 years; and the John T. Lewis & Bros. Company which manufactures the famous Dutch Boy White Lead has been operating in Philadelphia since 1772. Buckle molds similar to those of Revolutionary days are still in use. The Dutch process consists in exposing perforated sheets of lead "buckles" (Fig. 139) to the action of acetic acid vapor, moisture, and carbon dioxide. Small earthenware pots, each containing a shelf or ledge, are practically filled with dilute acetic acid (3–5 per cent acid) and on each shelf or ledge the perforated plates of lead are supported. The pots so charged are placed side by side upon a layer of moist spent tanbark which is ready to ferment. A board floor is supported a few inches above the pots, and upon this another layer of tanbark is spread. Other alternate layers of pots and tanbark are built up until an enormous shed is almost full, the doorway being boarded up as the filling continues. The heat liberated by the fermentation of the tanbark vaporizes acetic acid and water, which interact with lead, forming the basic lead acetate. The carbon dioxide formed by fermentation transforms the acetate into basic lead carbonate, or white lead. The vapor of acetic acid may be regarded as a catalyst, for it is regenerated and used over again. The action is slow, about three months being required for the process to complete itself.



*Courtesy of the National Lead Company*

FIG. 139. Steps in the old Dutch Process for manufacturing white lead.

The process is so time-consuming that rapid methods have been invented; but the conservative painter still insists on white lead made by the Old Dutch Process.

In the **Carter process** molten lead is first "atomized" by treating a stream of the molten metal with a blast of superheated steam or compressed air. The finely divided product is then treated with dilute acetic acid and carbon dioxide, in wooden cylinders which are revolved slowly. The time is shortened to about 15 days.

**401. Paint.**—White lead ground with linseed oil is used extensively as the **body** of paint. It has a greater covering power than zinc-white (ZnO, **361**), or permanent white (lithopone, $BaSO_4 + ZnS$, **353**) but turns dark in the presence of hydrogen sulfide in the air. 15 per cent $TiO_2$ is often admixed with it to form titanium-white paints. The paint body is suspended in oils (*e.g.*, linseed oil, tung oil) called the **vehicle**; and metallic-organic compounds (*e.g.*, of cobalt or manganese resinate) are added to hasten the oxidation and polymerization of the oil; they are called **driers.** If a colored paint is desired, a **pigment** such as red lead or chrome yellow is added. Painters occasionally have a violent form of intestinal colic known as "lead colic," later developing chronic lead poisoning. Paint manufacturers carefully guard against this colic in their factories, and require their workers to drink a quart of milk each day, which removes traces of lead from the body.

The pigments sold in the United States in 1939 were: lithopone, 142,750; zinc oxide, 114,552; white lead, 98,429; litharge 89,518; and red lead, 39,976 short tons.

The drying action of these paints involves chemical oxidation and polymerization of the vehicle; in a later section (535, *a*) this will be distinguished from the drying action of lacquers.

**402. Analysis of Group IV-B.**—The compounds of **tin** yield a metallic bead when heated on charcoal in the reducing flame. The metal is malleable and leaves a white insoluble residue when treated with nitric acid. The ions $Sn^{++}$ and $Sn^{++++}$ are colorless.

When a lead compound is heated on charcoal in a reducing flame, a bright malleable button of the metal is obtained. PbS is insoluble in ammonium polysulfide, which affords a means of separating lead from tin. The lead ion, $Pb^{++}$, is colorless and highly poisonous.

### DEMONSTRATION 116. ANALYSIS FOR TIN AND LEAD

Materials: Ten test glasses, solutions containing $Pb^{+2}$, $Sn^{+2}$, and $Sn^{+4}$, $(NH_4)_2Sn_x$, $H_2S$-water, HCl, $K_2Cr_2O_7$, $HgCl_2$, $H_2SO_4$.

In **routine qualitative analysis** lead is precipitated in Group I as lead chloride and in Group II as lead sulfide. The chloride is separated from AgCl and $Hg_2Cl_2$ by boiling in water, in which $PbCl_2$ alone is soluble. Lead is subsequently confirmed by adding $K_2Cr_2O_7$, which precipitates yellow $PbCrO_4$. In Group II black lead sulfide (PbS), brown stannous sulfide (SnS), and bright yellow stannic sulfide ($SnS_2$) are precipitated by $H_2S$ in 0.3 N acid solution. The tin sulfides are dissolved by boiling with yellow ammonium sulfide (ammonium polysulfide, $(NH_4)_2S_x$) which forms complex tin salts:

$$SnS_2 + (NH_4)_2S \rightarrow (NH_4)_2SnS_3$$
$$SnS + (NH_4)_2S_2 \rightarrow (NH_4)_2SnS_3$$

(ammonium thiostannate)

The tin is further identified by forming a stannous salt which will precipitate black Hg or white $Hg_2Cl_2$ when added to a solution of $HgCl_2$. The lead sulfide precipitate is separated from HgS, with which it precipitates, by boiling in concentrated nitric acid: the lead dissolves. It is then precipitated with sulfuric acid, and further identified by forming the insoluble yellow chromate, as above.

**403. Uses for Group IV Compounds.**—Carbon and silicon compounds are omitted.

TABLE 82. USES FOR GROUP IV COMPOUNDS

| | |
|---|---|
| **Group IV-A** | **titanium white, zirconium, hafnium, cerium, ceric sulfate, thorium (386).** |
| **Group IV-B** | **germanium, tin, lead (387–8).** |
| **Tin and its compounds** | **tin (389–92), alloys (392), $Sn(OH)_2$ (393); $SnO_2$, metastannic acid, sodium metastannate (394); stannic chloride (395).** |
| Ammonium chlorostannate, pink salt $(NH_4)_2SnCl_6$ | mordant for cotton. |
| Stannic sulfide $SnS_2$ | mosaic gold, gilt pigment. |
| Stannous chloride tin crystals, tin salt $SnCl_2, 2H_2O$ | white crystals; powerful reducing agent for organic syntheses; mordant; weighting silk; fire-retardant. |
| **Lead and its compounds** | **Pb (396–8), oxides, $Pb(OH)_2$ (399), white lead (400–1), lead in paint (401).** |
| Lead acetate, sugar of lead $Pb(CH_3COO)_2, 3H_2O$ | very soluble in water; medicine, mordant, weighting silk, manufacturing lead salts; solution has a sweet taste. |
| Lead arsenate $Pb_3(AsO_4)_2$ | white insecticide, not readily dissolved by rain. |
| Lead iodide $PbI_2$ | golden yellow; printing, photography, bronzing. |
| Lead pigments | $PbCrO_4$, chrome yellow; $PbTiO_3$, white; $PbCrO_4$, PbO Persian red; $PbMoO_4$, PbO, Ming orange; chrome green, a mixture of chrome yellow and Prussian blue (439). |
| Lead sulfate (basic) $PbSO_4$, PbO | sublimed white lead (4000 tons annually) 75% $PbSO_4$, 20% PbO, 5% ZnO as pigment; also blue variety; both from heating galena. |
| Lead tetraethyl, tetraethyl lead, $Pb(C_2H_5)_4$ | 1% in gasoline prevents premature explosion, *i.e.*, an anti-knock (Midgley); made from ethyl bromide plus sodium-lead alloy. |

## QUESTION REVIEW

I. GROUP IV-A. Ti, Zr, Hf, Ce, Th (386).

1. What demonstration illustrates that titanium is only weakly metallic?
2. Account for the fluctuation in titanium and monazite sand production during the past quarter-century.

II. GROUP IV-B. Ge, Sn, Pb (387–8).

III. TIN.

**a. History and occurrence (389). Metallurgy (390).**

3. What change in the composition of certain coins occurred near the middle of the second century B.C.?
4. Outline the metallurgy of tin. How is tin scrap treated?

**b. Properties (391). Uses (392).**

5. Why might it be unwise to take tin-canned goods on an arctic expedition?
6. Give equations showing the reaction of tin with two dilute and two concentrated acids. Of tin with potassium hydroxide.
7. What is the composition of (*a*) bronze, (*b*) a safety pin, (*c*) tin-plate?

**c. Stannous hydroxides (393). Stannic oxide and metastannic acid (394). Stannic chloride (395).**

8. Give equations involving both stannous and stannic compounds to demonstrate the weakly metallic properties of tin.

IV. LEAD.

**a. History and occurrence (396). Metallurgy (397).**

9. What is the chief ore of lead? Who are the principal world producers? How much more is produced in Missouri than in Idaho and Utah?
10. Give equations showing the metallurgy of lead.
11. How is lead refined (*a*) if silver is absent, (*b*) in the presence of silver, (*c*) by a process analogous to the refining of copper?

**b. Properties and uses of lead (398).**

12. The Romans used lead pipes. Could this have affected their health?

13. Account for the fact that lead is dissolved by acetic acid, but not by hydrochloric and sulfuric acids which are usually considered very active acids.

c. **Oxides and hydroxides** (399).

14. Draw a flow-sheet showing the relations in manufacturing various lead oxides.
15. What proof is there that red lead is not an oxide?
16. Write equations demonstrating the amphoteric nature of lead hydroxide.

d. **White lead** (400). **Paint** (401).

17. How is Dutch Boy White Lead manufactured? What evidence is there that the process is old?
18. What is the composition and function of each of the following: body, vehicle, pigment, drier.
19. What pigment is used in greatest quantity? What properties make it superior to other pigments?

V. ANALYSIS OF GROUP IV-B (402).

20. For what is each of the following used in the analysis of tin and lead: $H_2S$, $K_2Cr_2O_7$, $HCl$, $H_2SO_4$, $(NH_4)_2S_x$, reducing flame, $HgCl_2$?

VI. USES FOR GROUP IV COMPOUNDS (403).

21. Tabulate the names and uses for five compounds containing members of Group IV.

**Reading References:** Articles number 15, 50, 61, 112, 125, 231, 233 and 241 in the Appendix.

# CHAPTER XXX

## THE METALS OF SUB-GROUPS V-A, VI-A AND VII-A CHROMIUM AND MANGANESE

**404. Characteristics of these A-Sub-Groups.**—Of the A sub-groups, V-A, VI-A and VII-A remain to be taken up. Discussion of them will be brief since these elements have only a restricted interest, with the exception of chromium and manganese which will be taken up in some detail.

### GROUP V-A. THE VANADIUM FAMILY

**405. Group V-A.**—These members are listed in Table 83. Uranium $X_1$ has been mentioned in section 249.

TABLE 83. GROUP V-A. THE VANADIUM FAMILY

| Element | Atomic Weight | Atomic Number | Density | Melting Point | Boiling Point |
|---|---|---|---|---|---|
| Vanadium, V | 50.95 | 23 | 5.87 | 1715° | 3400° |
| Columbium, Cb | 93.1 | 41 | 8.4 | 1950° | >3300° |
| Tantalum, Ta | 180.88 | 73 | 16.6 | 2850° | >4100° |
| Uranium-$X_1$, $UX_1$ | (231) | 91 | — | — | — |

**a. Occurrence.** These elements occur chiefly in complex anions, including vanadinite, $Pb_5(VO_4)Cl$; columbite, $FeCb_2O_6$, which is often associated with tantalite, $FeTa_2O_6$; and carnotite $K_2O, 2UO_3, V_2O_5, 3H_2O$.

**b. Metallurgy.** Carnotite ores are roasted with salt, forming water-soluble sodium vanadate, $NaVO_3$; and addition of acid to this precipitates vanadium pentoxide, $V_2O_5$. Peru and the United States each produced about 1000 tons in 1939, two-thirds of the total world-production.

Columbite comes from Nigeria, and tantalite from Australia, only a few hundred tons of each being produced annually. The metals may be obtained with difficulty by reducing the oxides with calcium or aluminum. However, for making special alloys the free metal is not added: rather, the alloys ferrovanadium and ferrocolumbium are employed.

**c. Physical properties.** They have a steel-grey appearance; and although these metals are hard, they may be die-drawn and cold-rolled. Vanadium is employed for strengthening steel; columbium renders chromium-steel weldable; and tantalum is replacing platinum ware. Tantalum carbide is a cutting-tool alloy.

**d. Chemical properties.** When heated, V, Cb, and Ta are acted upon by oxygen. Though V dissolves in $HNO_3$, Cb and Ta are attacked only by a mixture of $HNO_3$ and HF.

They all have a valence of +5. Vanadium forms +2, +3, +4, and +5 valence states. The lower two are basic; the upper two, amphoteric. Columbium compounds with lower valences are quite unstable; and tantalum compounds with a valence of +2 do not even exist in water.

Many vanadium compounds are highly colored, *e.g.*, green vanadium dichloride, $VCl_2$; black sodium vanadite, $Na_2V_4O_9$; deep blue vanadyl sulfate, $VOSO_4$, and yellow ammonium vanadate, $NH_4VO_3$. The latter is manufactured in some quantity for making $V_2O_5$ as a catalyst for the sulfuric acid contact-process (585). No columbium salts of special importance are made. Tantalum forms compounds such as sodium fluotantalate, $Na_2TaO_7$, soluble in hot water; and sodium metatantalate, $NaTaO_3$, insoluble.

c. **Uses.** All three metals are used chiefly for special steels; although small quantities of vanadium are also consumed in the non-ferrous, glass, ceramic, and color industries, and as $V_2O_5$ catalyst in the contact process for sulfuric acid.

## GROUP VI-A. THE CHROMIUM FAMILY

### 406. General Characteristics of Group VI-A.—

TABLE 84. GROUP VI-A. THE CHROMIUM FAMILY

| Element | Atomic Weight | Atomic Number | Density | Melting Point | Boiling Point |
|---|---|---|---|---|---|
| *Chromium, Cr | 52.01 | 24 | 7.1 | 1615° | 2200° |
| Molybdenum, Mo | 95.95 | 42 | 10.2 | 2620° | 3700° |
| Tungsten, W | 183.92 | 74 | 19.3 | 3370° | 4727° |
| Uranium, U | 238.07 | 92 | 18.7 | >1850° | — |

* Planetary arrangement $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$.

The members are metals with high melting points, tungsten having the highest melting point of any metal. They form tough alloys. All have a maximum valence of +6, forming compounds corresponding to the sulfates; and the oxides with the formula $MO_3$ are acidic in nature:

| *Anhydride* | *Acid* | *Salt* |
|---|---|---|
| $CrO_3$ | Chromic, $H_2CrO_4$ | Potassium chromate, $K_2CrO_4$ |
| $MoO_3$ | Molybdic, $H_2MoO_4$ | Ammonium molybdate, $(NH_4)_2MoO_4$ |
| $WO_3$ | Tungstic, $H_2WO_4$ | Sodium tungstate, $Na_2WO_4$ |
| | | *compare* |
| $SO_3$ | Sulfuric, $H_2SO_4$ | Sodium sulfate, $Na_2SO_4$ |

They have one striking characteristic: **the formation of polyacids,** giving rise to compounds such as ammonium phosphomolybdate, $(NH_4)_3PO_4$, $12MoO_3$, which is used in chemical analysis; and phosphotungstic acid, $H_3PO_4$, $12WO_3$, which is used to coagulate proteins and alkaloids.

Since they do not closely resemble one another, they will be taken up individually. On the other hand, each member is remarkably similar to the element immediately preceding and that immediately following it in atomic number. For this reason, **chromium and manganese (atomic numbers 24 and 25) will be considered together, in detail, later in the chapter.**

**407. Molybdenum.**—This metal was isolated by Hjelm in 1783.

For most purposes it is produced as ferro-molybdenum by treating the ore, **molybdenite,** $MoS_2$, in an electric furnace with coke and iron. As a source of molybdenum compounds molybdenite is roasted with lime, forming soluble calcium molybdate, $CaMoO_4$.

In 1939, 66 per cent of the world's molybdenite came from the Climax, Colorado mine, the United States accounting for 92 per cent (13,755 tons) of the metal produced.

During the past decade the use of molybdenum high-speed steel has been increasing. A typical steel of this type contains 9 per cent Mo, 1 per cent W, 1 per cent V, 4 per cent Cr, and the remainder ordinary steel. Molybdenum is substituted for the more expensive tungsten in radio tubes where it is not subjected to heat.

Molybdenite when roasted forms white molybdenum trioxide, $MoO_3$, which is sparingly soluble in water, forming molybdic acid, $H_2MoO_4$ (compare $SO_3$ and $H_2SO_4$).

**Ammonium molybdate,** $(NH_4)_2MoO_4$, is formed when $MoO_3$ is heated with an excess of concentrated ammonia. When phosphoric acid is treated with a solution of ammonium molybdate in the presence of nitric acid, a yellow precipitate of **ammonium phosphomolybdate,** $(NH_4)_3PO_4$, $12MO_3$, $xH_2O$, is obtained. Ammonium molybdate is therefore used in the detection and separation of phosphoric acid. The compound also is used in the dyeing of silk.

**408. Tungsten.**—Tungsten (Swedish, heavy-stone) was discovered by Scheele in 1781. Its symbol, W, comes from the German name for it, *wolfram.*

**Metallurgy.**—Tungsten is formed as a brown powder upon reducing $WO_3$ with carbon, aluminum or hydrogen. The $WO_3$ is obtained from wolframite (Fe, Mn) $WO_4$, by the following process: the ore is roasted with sodium carbonate, forming water-soluble sodium tungstate, $Na_2WO_4$, $2H_2O$; this in turn is acidulated with HCl to form tungstic acid, $H_2WO_4$, $H_2O$; and the latter upon ignition yields $WO_3$. **Ferro-tungsten** alloy is produced by the direct reduction of wolframite containing a low percentage of manganese.

World production in 1939 was approximately 43,000 metric tons containing 60 per cent $WO_3$. China originally produced nearly half the world's supply; but the Sino-Japanese hostilities cut shipments nearly in half, and production in the United States increased.

**Properties and Uses.**—Tungsten is a steel-grey, very hard metal, density 19.3, melting point higher than any other metal, 3370°.

Tungsten does not rust and is not attacked by nitric, hydrochloric, or sulfuric acid; it dissolves very readily, however, in a mixture of nitric and hydrofluoric acids. At high temperatures, it combines with oxygen and with nitrogen.

Working, hammering and drawing a metal often changes its properties. Manganese steel grows harder under such a treatment; tungsten metal on the other hand becomes more ductile. This principle is utilized in making **lamp filaments** for electric lights. The tungsten powder obtained by the reduction of $WO_3$ by hydrogen is heated again in an electric furnace to form a rod. The rod is then worked again and again until it is ductile enough to be drawn through a diamond die as a fine thread possessing unusual strength.

**High-speed tool-steel** possesses the property of keeping its temper even at red heat: this makes possible the mass production of parts cut out of metals on the lathe. Tungsten steels possess just this property; and tungsten is, therefore, a strategic material. The most common tungsten-steel contains 18 per cent W, 4 per cent Cr, 1 per cent V and the remainder iron and carbon.

Tungsten also is used for targets and cathodes of X-ray tubes, for electric contacts in explosion engines, in special alloys, in mordants, and in minor chemicals.

**Compounds.**—Tungsten forms compounds with valences +2 through +6, although the +6 compounds are the important ones. Polytungstates of the form $(Na_2O)_a(WO_3)_b$ exist; if $a = 1$, $b$ may vary from 1 to 6. Tungstates are, with the exception of a few alkali tungstates such as $Na_2WO_4$, $2H_2O$, insoluble in water.

**409. Uranium.**—Klaproth, who discovered uranium in pitchblende in 1789, named the element in honor of Herschel's discovery of the planet Uranus (1781).

The enormous deposits of pitchblende which were uncovered in the Canadian Northwest in 1930 are described in section 247. Uranium also occurs in **carnotite,** $K_2O$, $2UO_3$, $V_2O_5$, $3H_2O$, which is also a vanadium ore. The metal was not isolated until 1842, when Peligot reduced uranium tetrachloride with potassium.

**Metallurgy.**—It may be prepared by heating $U_3O_8$ with sugar charcoal in an electric furnace.

Uranium is extracted from pitchblende by roasting the $U_3O_8$ with sodium carbonate, giving sodium uranate, $Na_2U_2O_7$; and this is converted into uranyl sulfate, $UO_2SO_4$.

**Properties.**—Uranium undergoes oxidation with the air, dissolves in acids to form salts, decomposes water, and unites with chlorine, sulfur and nitrogen. It is radioactive (247).

Uranium possesses valences from +2 through +6; but only the +4 and +6 valence states are stable in water. The most common salts of uranium contain the **uranyl radical,** $UO_2$, in which the radical plays the rôle of a bivalent metal: *e.g.*, **uranyl nitrate,** $(UO_2)(NO_3)_2$, $6H_2O$, and **uranyl sulfate,** $(UO_2)SO_4$, $3H_2O$. These are beautiful yellow salts. The dioxide $UO_2$ is basic, and $UO_3$ is uranic anhydride. $U_3O_8$ is the most stable of its oxides.

**Uses.**—Compounds of uranium are used to impart a yellowish-green fluorescence to glass, as well as in china painting to produce a velvety black color. They are also used in the dye industry. Most of the uranyl salts are strongly fluorescent.

## GROUP VII-A. THE MANGANESE FAMILY

### 410. Group VII-A.—The members are listed below.

TABLE 85. THE MANGANESE FAMILY

| Element | Atomic Weight | Atomic Number | Density | Melting Point | Boiling Point |
|---|---|---|---|---|---|
| *Manganese, Mn | 54.93 | 25 | 7.2 | 1260° | 1900° |
| Masurium, Ma | ? | 43 | only identified in X-ray spectra | | |
| Rhenium, Re | 186.31 | 75 | 20.53 | 3440° | — |

* Planetary arrangement $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$ *i.e.*, 2–8–(8 + 5)–2.

Manganese is a relatively abundant element, constituting 0.08 per cent of the earth's crust. On the other hand, we know little about masurium beyond Noddack's observation (1925) of X-ray lines corresponding to element number 43. Noddack also discovered rhenium (1925). This metal has been produced commercially in Germany in small quantities, for use in radio and power tubes; and a number of manganese minerals in Arkansas have been found to contain traces of rhenium.

These elements form valence states from +2 through +7. Again, like the members of group 6, they resemble the elements in adjacent groups (*e.g.*, Mn is like Cr and Fe). There is also some analogy in the +7 state with the VII-B members: $Cl_2O_7$, $Mn_2O_7$ and $Re_2O_7$ are considered the acid anhydrides of the per-acids $HClO_4$, perchloric acid; $HMnO_4$, permanganic acid; and $HReO_4$, per-rhenic acid.

### CHROMIUM AND MANGANESE. (VI-A AND VII-A)

**411. History and Occurrence.**—

**Chromium.** This element (Greek *chroma*, meaning color, since all chromium compounds are colored) was known to exist in the mineral crocoite, $PbCrO_4$, as early as 1797 (Vauquelin). Metallic chromium was prepared by Deville in 1857, who reduced the oxide $Cr_2O_3$ with carbon at a very high temperature. Wöhler obtained it by reducing the chloride with zinc, and then treating the alloy with nitric acid.

Chromium ore, **chromite,** FeO, $Cr_2O_3$, is the chief ore of chromium; the commercial ore usually contains about 35 per cent $Cr_2O_3$. 1,125,000 metric tons of crude chromite was produced in 1938; of this 213,630 came from Turkey, 186,019 from Southern Rhodesia, and approximately 50,000 tons each from Canada, Greece, New Caledonia, Philippine Islands and Yugoslavia.

**Manganese.** This element was first isolated by Gahn in 1774 from pyrolusite (Latin *magnes*, because of its resemblance to magnetite). It is widely distributed as oxides, silicates and carbonates, constituting 0.08 per cent of the earth's crust; and the black ore, **pyrolusite,** $MnO_2$, is its chief source.

5,108,000 tons of manganese ore containing over 35 per cent manganese was mined in 1938. Russia accounted for 45 per cent of world production, India and Africa about 20 per cent each, while Cuba and Brazil produced approximately 100,000 tons each. Domestic ore is of inferior grade. A special grade of pyrolusite which must contain not less than 70 per cent $MnO_2$ and not more than 2 per cent iron is required for dry cells. 7767 tons of this ore was shipped to the United States in 1939, principally from the African Gold Coast.

**412. Metallurgy.**—Chromium and manganese are prepared by similar methods.

**a. Goldschmidt process.** The oxide is mixed with finely divided aluminum, and the combustion started with magnesium; so much heat is given off that the temperature rises to 3000°, and a fused mass of metal separates out from an alumina slag:

$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3 + 122{,}000 \text{ cals.},$$
$$3MnO_2 + 4Al \rightarrow 3Mn + 2Al_2O_3.$$

**b. Carbon reduction.** Ores containing iron-chromium or iron-manganese are reduced with carbon in the electric furnace:

$$Cr_2O_3, FeO + 4C \rightarrow Fe, 2Cr + 4CO \uparrow,$$
$$MnO_2, FeO + 3C \rightarrow Fe, Mn + 3CO \uparrow,$$

The products are alloys of the metals with iron, called **ferrochromium** and **ferromanganese.** These alloys are added to molten iron in making special steels. Ferrochromium contains 60 to 70 per cent chromium and 2 to 4 per cent carbon, depending upon the type of steel desired. Ferromanganese contains about 80 per cent manganese; the bulk of the manganese ore entering this country is converted into ferromanganese. Domestic ore is inferior, and is made into **spiegeleisen,** another iron-manganese alloy containing considerably less than 10 per cent manganese. See table 94, section 435.

**413. Properties and Uses.**—As is attested by its use in the automotive industry, chromium takes a high polish; manganese is grey like cast iron. Chromium and manganese have nearly equal densities (Cr 7.1, Mn 7.2); and their melting points are relatively low (Cr 1615°, Mn 1260°), manganese having the lowest melting point of any steel-forming metal. The metals may be distilled in the electric furnace, the boiling points being Cr 2200°, Mn 1900°.

Chromium burns in the oxyhydrogen flame more brilliantly than iron, forming green $Cr_2O_3$; but unlike manganese it does not oxidize readily in the air. Above 1210° manganese combines rapidly with nitrogen. Both manganese and chromium react slowly with dilute hydrochloric or sulfuric acid to form *ous*-salts; but chromium is not dissolved by concentrated nitric acid: this is due to its becoming "passive," a phenomenon likewise exhibited by iron but little understood.

**Special steels** followed the discovery by Hadfield in 1882 that a few per cent of **manganese** increased the hardness of ordinary steel; and that a manganese steel became harder the more it was worked. Besides increasing the toughness of steel, manganese acts as a deoxidizer as well as a medium for the introduction ot the requisite amount of carbon. **Chromium alloys** are the basis for stainless steels. A number of other chromium and manganese alloys are tabulated in section 435. **Chromium plate** is achieved by electrolysis of a chromic acid solution; a typical formula is 250 g. of $CrO_3$ plus 3.3 g. of $Cr_2(SO_4)_3$ per liter of solution.

**414. Valence States of Cr and Mn.**—Table 86 summarizes the valence states exhibited by these two metals. The relatively unimportant *ites* have been omitted from the chart for simplicity: in these, chromium is +3 and manganese +4, *viz.*, $NaCrO_2$, sodium chromite; $Na_2MnO_3$, sodium manganite.

TABLE 86. SOME VALENCE STATES OF CHROMIUM AND MANGANESE

| +2 (OUS) | +3 (IC) | +6 (ATE) | +7 (PER . . . ATE) |
|---|---|---|---|
| **Chromous**<br>Unstable; less important than *ic*; powerful reducing agents going from $Cr^{++}$ to $Cr^{+++}$; like $Fe^{++}$.<br>$CrCl_2$ . . . chromous chloride; $Cr(OH)_2$ chromous hydroxide oxidizes to chromic hydroxide. | **Chromic**<br>Stable; more important than chromous, highly hydrolyzed; all soluble excepting oxide, hydroxide, phosphate; $Cr^{+++}$ purple.<br>$Cr_2O_3$ stable, green; $Cr(OH)_3$ stable, green, several modifications known. | **Chromate**<br>**Dichromate**<br>$PbCrO_4$ lead chromate; $K_2Cr_2O_7$ potassium dichromate; $(CrO_4)^{=}$ yellow; $(Cr_2O_7)^{=}$ orange; $CrO_3$ and $(CrO_4)^{=}$ analogous to $SO_3$ and $(SO_4)^{=}$; powerful oxidizing agents. $H_2CrO_4$ not prepared. | **Perchromate**<br>Unstable; blue coloration formed from $H_2O_2$ + $K_2Cr_2O_7$; blue concentrated in ether layer.<br>Valence of blue perchromate not known. |
| **Manganous**<br>Stable; more important than manganic; $Mn^{++}$ pale-pink; does not oxidize in air like $Fe^{++}$ or $Cr^{++}$; analogous to $Mg^{++}$. | **Manganic**<br>Unstable, *i.e.*, $2MnCl_3 \rightarrow 2MnCl_2 + Cl_2$; analogous to, but more unstable than ferric salts; less important than manganous; highly hydrolyzed. | **Manganates**<br>Hydrolyze more readily than chromates or sulfates; $(MnO_4)^{=}$ green.<br>$Na_2MnO_4$, sodium manganate. $H_2MnO_4$ not prepared. | **Permanganates**<br>Stable; powerful oxidizing agents; $(MnO_4)^{-}$ deep purple; $KMnO_4$, potassium permanganate. |

Strangely enough these very valences are the ones possessed by the two chief ores of chromium and manganese: $Fe(CrO_2)_2$, ferrous chromite, and $MnO_2$, manganese dioxide or pyrolusite.

### 415. Preparation of Cr and Mn Compounds.—

**a. Ous-compounds.**—Chromous salts are prepared by dissolving chromium metal in dilute acids, or by reducing chromic salts with zinc. The manganous salts are prepared by treating manganous oxide, MnO, with the corresponding acids.

$$2CrCl_3 + Zn \rightarrow 2CrCl_2 + ZnCl_2.$$
$$MnO + 2HCl \rightarrow MnCl_2 + H_2O.$$

**b. Ic-compounds.**—These are obtained by the oxidation of the *ous*-compounds or reduction of the *ate*-compounds.

In **chrome tannage,** the skins, after appropriate preliminary treatment, are further treated with a solution of potassium (or sodium) dichromate and other chemicals, one of which is a reducing agent. Chromium hydroxide, $Cr(OH)_3$, is formed by reduction, and is precipitated in the leather. The skin is colloidal and the hydroxide is adsorbed. It is a rapid process, requiring only a few hours. It is employed chiefly for glove leathers, calf skin, and glazed kid.

**c. Ate-compounds.**—Manganates and chromates are prepared by heating the oxides with alkali carbonates (or hydroxides) in the presence of air (or an oxidizing agent, *e.g.*. $KNO_3$). In industry lime is likewise added to keep the mass porous and accessible to air.

$$\underset{\text{chromite}}{4FeOCr_2O_3} + 8K_2CO_3 + 7O_2 \rightarrow \underset{\text{pot. chromate}}{8K_2CrO_4} + 8CO_2 \uparrow + 2Fe_2O_3,$$

$$\underset{\text{pyrolusite}}{2MnO_2} + 2K_2CO_3 + O_2 \rightarrow \underset{\text{pot. manganate}}{2K_2MnO_4} + 2CO_2 \uparrow .$$

The manganates and chromates are analagous to the sulfates, and salts of the three are isomorphous, *i.e.*, $Na_2MnO_4$, $10H_2O$ and $Na_2CrO_4$, $10H_2O$, and $Na_2SO_4$, $10H_2O$ crystallize together. The acids $H_2CrO_4$ and $H_2MnO_4$ (corresponding to $H_2SO_4$) are too unstable to prepare.

The manganates and chromates are stable only in the presence of excess alkali; when potassium chromate is treated with sulfuric acid, **potassium dichromate,** $K_2Cr_2O_7$ is formed:

$$\underset{\text{yellow}}{2K_2CrO_4} + H_2SO_4 \rightarrow \underset{\text{orange}}{K_2Cr_2O_7} + K_2SO_4 + H_2O.$$

Industrially this is carried out with a saturated solution of the chromate; and the dichromate, which is less soluble than the sulfate, separates out as red, triclinic, *anhydrous* crystals. The corresponding sodium salt contains water of crystallization, $Na_2Cr_2O_7, 2H_2O$. Sodium or potassium hydroxide change the dichromate back into the chromate:

$$\underset{\text{orange}}{Cr_2O_7^{=}} + OH^- \rightarrow 2\underset{\text{yellow}}{CrO_4^{=}} + H^+.$$

**Chromic anhydride,** $CrO_3$, which bears the same relation to $K_2CrO_4$ that $SO_3$ does to $K_2SO_4$, is an important oxidizing agent. **Cleaning solution** which is often used to rid laboratory glassware of organic matter (grease) is prepared by treating a cold, saturated solution of potassium dichromate with concentrated sulfuric acid. $CrO_3$ separates out as scarlet needles.

$$K_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2KHSO_4 + \underset{\displaystyle 2CrO_3 + H_2O.}{\underset{\downarrow}{H_2Cr_2O_7}}$$

**d. Per-compounds.**—When an acidulated solution of a dichromate is treated with hydrogen peroxide a blue coloration appears; this may be extracted with ether which forms a blue top layer. A perchromate forms; the exact valence of chromium in this compound has not yet definitely been established. This is a delicate test for either hydrogen peroxide or the dichromate ion.

**Potassium permanganate** is a very important industrial product. Of the two formation methods given below, the oxidation with ozone is the one used industrially since there is no loss of Mn in the process:

$$\begin{aligned} 3K_2MnO_4 + 2CO_2 &\rightarrow 2KMnO_4 + 2K_2CO_3 + MnO_2, \\ 2\underset{\text{(green)}}{K_2MnO_4} + \underset{\text{(ozone)}}{O_3} + H_2O &\rightarrow \underset{\text{(purple-red)}}{2KMnO_4} + O_2 + 2KOH. \end{aligned}$$

Potassium permanganate forms purple crystals with a greenish luster, which are isomorphous with potassium perchlorate, $KClO_4$. The salt is readily soluble in water, forming a deep purple solution, due to the permanganate ion, $MnO_4^-$. It is a powerful oxidizing agent and is largely used as such.

When pure $KMnO_4$ is gradually added to well-cooled concentrated sulfuric acid, the salt dissolves, forming an olive-green solution. By cooling the solution and carefully adding water, **manganese heptoxide,** $Mn_2O_7$, separates out as a reddish-brown oily liquid; it is very unstable, a powerful oxidizing agent, and is the anhydride of permanganic acid:

$$2HMnO_4 \rightleftarrows H_2O + Mn_2O_7.$$

Manganese heptoxide is explosive, and it ignites paper and other organic substances (see $HClO_4$ and $Cl_2O_7$).

**416. Volumetric Analysis; Oxidation with Dichromates and Permanganates.**—These substances are powerful oxidizing agents, and are used as such in the textile industry, in organic syntheses, and in analytical chemistry. During the course of the oxidation reaction

(a) **permanganates in acid solution change to manganous salts, i.e., $(MnO_4)^- \rightarrow Mn^{++}$**

(b) **permanganates in neutral or alkaline solutions precipitate as manganese dioxide i.e., $(MnO_4)^- \rightarrow MnO_2 \downarrow$**

(c) **dichromates in acid solutions change to chromic salts, i.e., $(Cr_2O_7)^= \rightarrow Cr^{+++}$**

Typical oxidizing reactions are given below.

(a) **Analysis of iron** is frequently carried out by the use of these reagents. The iron is put into solution in the ferrous state, and the quantity of dichromate or permanganate required to oxidize it up to the ferric state is determined.

### DEMONSTRATION 117. TITRATION WITH PERMANGANATE

Materials: Three 400 cc. beakers, 25 cc. pipette, 0.1 or 0.2N ferrous sulfate, 0.1N $KMnO_4$, 3 stirring rods, 50 cc. burette clamped into position, white paper or porcelain plate, 1N $H_2SO_4$.

To determine the strength of the ferrous sulfate solution a **volumetric analysis** is made using the equipment shown on page 197. Twenty cc. of the ferrous sulfate (of unknown strength) is diluted to several hundred cc., and about 10 cc. of acid is added. Then 0.1N permanganate solution is run in from the burette drop by drop. The purple permanganate disappears immediately in accordance with the reaction:

$$\underset{\text{purple}}{2KMnO_4} + 10FeSO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + \underset{\text{(nearly colorless)}}{5Fe_2(SO_4)_3}.$$

After a quantity of $KMnO_4$ equivalent to the $FeSO_4$ (*i.e.*, 2 moles $KMnO_4$ for every 10 moles of $FeSO_4$) has been added, a single drop of $KMnO_4$ in excess turns the solution purple. This is the **end-point of the titration.** The volume of $KMnO_4$ is recorded. If, for example, 25 cc. of the unknown ferrous sulfate solution requires 50 cc. of 0.1N permanganate, the former is obviously twice as strong (*i.e.*, 0.2N) as the permanganate. Using the unknown ferrous sulfate solution given in Demonstration 117, we shall determine its strength.

(b) **In alkaline solutions $KMnO_4$ precipitates $MnO_2$.** Thus in the titration of manganous salts we have:

$$\underset{\text{pink}}{3MnSO_4} + \underset{\text{purple}}{2KMnO_4} + 2H_2O \rightarrow \underset{\text{brown ppt.}}{5MnO_2} \downarrow + \underset{\text{colorless}}{K_2SO_4} + 2H_2SO_4.$$

(c) **In titrations involving dichromate,** the orange dichromate ion turns to green chromic ion; since this is not a satisfactory color change, an **oxidation indicator** is added; this is oxidized to some distinctive color at the end-point (the organic compound diphenylamine, for example, turns blue).

**417. Step-wise Method for Balancing Equations.**—Elaborate oxidation-reduction equations such as the foregoing are easily balanced by the electron method (134) or by the following method.

*Step 1.* Write down the skeleton of the reaction:

$$K_2Cr_2O_7 + FeSO_4 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + H_2O + Fe_2(SO_4)_3 + K_2SO_4.$$

*Step 2.* Write down the elements or groups undergoing change

$$2Cr^{+6} + 7O^{-2} + Fe^{+2} \rightarrow 2Cr^{+3} + H_2O + 2Fe^{+3}.$$

*Step 3.* Balance each item both as regards number of atoms and number of electrons. Write electrons always as $+e$. Form $H_2O$ with oxygen or hydrogen.

$$\begin{aligned}
&(a) \quad & 2Cr^{+6} + 6e &\rightarrow 2Cr^{+3},\\
&(b) \quad & 7O^{-2} + 14H^{+} &\rightarrow 7H_2O,\\
&(c) \quad & 2Fe^{+2} &\rightarrow 2Fe^{+3} + 2e.
\end{aligned}$$

*Step 4.* Increase (*c*) so that its electrons balance those in (*a*)

$$\begin{aligned}
2Cr^{+6} + 6e &\rightarrow 2Cr^{+3},\\
7O^{-2} + 14H^{+} &\rightarrow 7H_2O,\\
6Fe^{+2} &\rightarrow 6Fe^{+3} + 6e.
\end{aligned}$$

*Step 5.* Substitute these values in the above skeleton

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 7H_2O + 3Fe_2(SO_4)_3 + K_2SO_4.$$

**418. Analysis for Chromium and Manganese.—Chromium salts may usually be recognized by their colors. Their borax bead test is emerald-green. Fusion with sodium carbonate-sodium nitrate gives yellow chromate. Manganese heated on a platinum foil with a mixture of sodium carbonate and sodium nitrate gives green manganate. Borax bead is amethyst-red in the oxidizing flame, colorless in the reducing flame.**

### DEMONSTRATION 118. ANALYSIS FOR Cr AND Mn

Materials: Eight test glasses, 200 cc. beaker over burner, large test-tube, solutions of $K_2Cr_2O_7$, $Pb(NO_3)_2$, $(NH_4)_2S$, $H_2O_2$, ether, conc. $HNO_3$, solid $PbO_2$, $MnO_2$, $MnCl_2$.

In this routine qualitative analysis chromium and manganese are precipitated in Group III with ammonium sulfide as green chromic hydroxide, $Cr(OH)_3$ and flesh-colored manganous sulfide, MnS, $xH_2O$. They are separated by forming soluble sodium chromate and insoluble manganese dioxide. The chromate is identified by its yellow color and by oxidation with $H_2O_2$ to blue perchromate (415, d). The manganese dioxide is dissolved in concentrated $HNO_3$ and subsequently identified by boiling with $PbO_2$ in nitric acid, which forms purple permanganate:

$$2MnO_2 + 3PbO_2 + 6HNO_3 \rightarrow 3Pb(NO_3)_2 + 2H_2O + \underset{\text{purple}}{2HMnO_4}.$$

**419.**—

TABLE 87. USES FOR COMPOUNDS OF GROUPS V-A, VI-A, AND VII-A.

| | |
|---|---|
| **Alloys** | **ferrochromium, ferromanganese, spiegeleisen** (412). |
| Carboloy | $W_2C$, tungstic carbide; hardness lies between diamond and sapphire. |
| Chrome steel | dense, tough; crushers, armor plate, cutting tools. |
| Manganese bronze | resists corrosion; propeller blades. |
| Manganin | Cu-Ni-Mn; standard resistance wire. |
| Nichrome Cr-Ni-Fe | small electric furnace windings since it does not oxidize and has a high melting point. |
| Stainless steel | 12 per cent Cr, 0.3 per cent C, remainder Fe. |
| Tungsten steel | 15 per cent W, 4 per cent Cr, 1 per cent V remainder Fe and C. High speed tools. |
| Stellite W-Co-Cr | retains temper at red heat; cutlery, high-speed tools. |
| **Group V-A** | **V, Cb, Ta, $UX_1$, $NH_4VO_3$, $V_2O_5$ (405).** |
| **Group VI-A** | **Cr, Mo, W, U; $(NH_4)_3$, $PO_4$, $12MoO_3$; $H_3PO_4$, $12WO_3$ (406); $MoS_2$; $(NH_4)_2MoO_4$ (407); W (408); U, uranyl compounds (409).** |
| Molybdate orange $PbMoO_4$, PbO | Ming orange; orange pigment similar to chrome orange. |
| Sodium molybdate | $Na_2MoO_4$; staining leather, coloring pottery blue. |
| Sodium tungstate | $Na_2WO_4$; fireproofing fabrics, mordant. |
| Tungsten lakes | organic dyes plus acidified sodium tungstate forming brilliant printing inks. |
| Tungstic acid $H_2WO_4$ | also wolframic or orthotungstic acid; yellow powder; mordant; in plastics; for W wire. |
| Uranium oxide $U_3O_8$ | pitchblende; fluorescent glass, coloring porcelain, catalyst, preparing uranium salts. |
| **Group VII-A** | **Mn, Ma, Re (410).** |

TABLE 87.—*continued*

| | |
|---|---|
| **Chromium and its compounds** | **Cr, (411); $Cr_2O_3$, Cr-plate (413); chromite, $CrO_3$, $K_2Cr_2O_7$, $Cr(OH)_3$ (415).** |
| Chrome alum $K_2SO_4$, $Cr_2(SO_4)_3$, $24H_2O$ | potassium chrome alum; violet-red crystals; mordant and printing inks. |
| Chrome yellows | $PbCrO_4$ or $ZnCrO_4$ or $BaCrO_4$ as base. |
| Chromic acetate $Cr(CH_3COO)_3$, $H_2O$ | mordant; dyeing and printing textiles. |
| Chromic fluoride $CrF_3$, $4H_2O$ | green powder; printing, dyeing, color for stones. |
| Chromic oxide $Cr_2O_3$ | do not confuse with chrome green (prussian blue and lead chromate); pigment; green glass. |
| Chromic sulfate $Cr_2(SO_4)_3$, $15H_2O$ | mordant; basic sulfate for tanning. |
| Ferrous chromite | $Fe(CrO_2)_2$; chromite ore; refractory. |
| **Manganese and its compounds** | **Mn, $MnO_2$, ferromanganese, spiegeleisen (411–2); $KMnO_4$, $Mn_2O_7$ (415).** |
| Condy's fluid | disinfecting fluid containing $Al(MnO_4)_3$ which hydrolyzes forming permanganic acid, $HMnO_4$. |
| Manganous acetate $Mn(CH_3COO)_2$, $4H_2O$ | soluble in water, pink; drier, leather, mordant, catalyst. |
| Manganous chloride $MnCl_2$, $4H_2O$ | red, deliquescent; preparation of catalysts; dyeing. |
| Manganous driers | organic linoleate, resinate, etc. |
| Manganous sulfate $MnSO_4$, $7H_2O$ | pink crystals; plant stimulant. |

## QUESTION REVIEW

I. GROUP V-A: V, Cb, Ta, $UX_1$ (405).

1. What effect does each of these elements have on steel?
2. Contrast valence states of the elements.

II. GROUP VI-A (406). Mo (407), W (408), U (409).

3. Outline the general characteristics of the members. What striking property do they all possess?
4. Identify some fact with each of the following: $WO_3$; $MoS_2$; (Fe, Mn)$WO_4$; $H_2WO_4$, $H_2O$; ammonium phosphomolybdate; ferrotungsten; $Na_2WO_4$, $2H_2O$; $MoO_3$; uranyl radical; $U_3O_8$; carnotite.

III. GROUP VII-A: Mn, Ma, Re (410).

5. Discuss masurium and rhenium.

IV. CHROMIUM AND MANGANESE (Groups VI-A and VII-A).

a. **History and occurrence (411). Metallurgy (412).**

6. What countries supply these important metals? What ores are there?
7. When is C preferred to Al in the reduction of ores of these two metals?
8. Why is not ferromanganese produced from domestic ores?

b. **Properties and uses (413).**

9. State their physical and chemical properties.
10. What special property does manganese impart to steel? What property does chromium impart?

c. **Valence states (414).**

11. Prepare a chart showing the various valence states represented by these two metals.

d. **Preparation of compounds: ous, ic, ate, per-ate (415).**

12. How would you prepare each of the following: $MnSO_4$; $Cr(NO_3)_3$; $Cr(OH)_3$; $Na_2CrO_4$, $10H_2O$; $(NH_4)_2Cr_2O_7$; $CrO_3$; $NaMnO_4$?

e. **Volumetric analysis: oxidation with dichromates and permanganates (416). Balancing equations (417).**

13. What is the normality of a ferrous sulfate 20 cc. of which exactly neutralizes (*a*) 20 cc. of 0.1N dichromate, (*b*) 40 cc. of 0.1N permanganate, (*c*) 14 cc. of 2N dichromate, (*d*) 30 cc. of 0.5N permanganate.

14. Balance the following equations.
    - *a.* $K_2Cr_2O_7 + H_2SO_4 +$ ferrous nitrate →
    - *b.* $KMnO_4 + HCl +$ stannous chloride →
    - *c.* $KMnO_4 + FeSO_4$ in neutral solution →
    - *d.* $K_2Cr_2O_7 + H_2SO_4 + CH_3OH \rightarrow$ (latter forms $HCOOH$)

### f. Analysis for chromium and manganese (418.)

15. How do the following enter into the analytical scheme: $PbO_2$, $Cr(OH)_3$, borax bead, perchromate, permanganic acid; $MnS, xH_2O$; $(NH_4)_2S_x$?

## V. USES FOR COMPOUNDS OF GROUPS V-A, VI-A AND VII-A (419).

16. Name and give a use for 10 compounds.

**Reading References:** Articles number 20, 61, 70, 102, 130, 203, 204, 214, 221, 228 and 252 in the Appendix.

# CHAPTER XXXI

# IRON AND STEEL

**420. Historical.**—By 1000 B.C. ancient man had made use of stone, bronze, meteoritic and metallurgical iron. Although experts are not in agreement as to the exact dates for these Ages of Man, it is likely that the smelting of bronze preceded the smelting of iron, since the latter requires a higher temperature. It is certain, however, that iron was employed by the ancient world.

**421. Occurrence.**—Next to aluminum (8.1 per cent) the most abundant metal in the earth's crust is iron (5.1 per cent). In the free state considerable masses are found in Greenland, probably of meteoritic origin. It is an essential constituent of hemoglobin: if the blood-count (*i.e.*, the number of hemoglobin-containing, red, blood-corpuscles) is low, the patient is anemic and more susceptible to disease.

In the combined state, iron occurs in many minerals; **hematite,** $Fe_2O_3$, which accounted for 97 per cent of all our domestic ore in 1939; **limonite,** $2Fe_2O_3$, $3H_2O$, abundant in the Alabama region, and the chief ore of France and Germany; and **magnetite,** $Fe_3O_4$, richest of iron ores (72.4 per cent Fe), from above the arctic circle in Sweden, and in the Eastern United States; **siderite,** $FeCO_3$; and **iron pyrites,** $FeS_2$, which is usually not an ore because of the difficulty of removing the sulfur. Statistics on these ores are given in Table 88.

TABLE 88. IRON ORE IN THE UNITED STATES (1939); gross tons

| **Types of ore** | | **Districts worked** | |
|---|---|---|---|
| Hematite | 47,756,770 | Lake Superior | 41,679,608 |
| Limonite | 598,372 | Alabama | 5,734,688 |
| Magnetite | 3,377,764 | | |
| Siderite | 463 | **Methods of mining** | |
| | | Open pit | 32,741,636 |
| **total**............ | **51,721,369** | Underground | 18,979,733 |

**422. Metallurgy of Iron and Steel.**—Common iron is quite unsatisfactory for the demands of our present civilization. By controlling the quantity of carbon which is left in the iron during the reduction process, a **steel** is produced. Unlike iron, steel can be rendered very hard by heating to critical temperatures and suddenly cooling (*i.e.*, tempering); also, it can be welded and forged. Moreover, a few per cent of certain metals (*e.g.*, W, Mn, Cr) added to the iron produces steels which are especially hard, or resist corrosion, or have unusual strength. The steps by which the raw iron ore is converted into these various products is shown diagrammatically in Fig. 140.

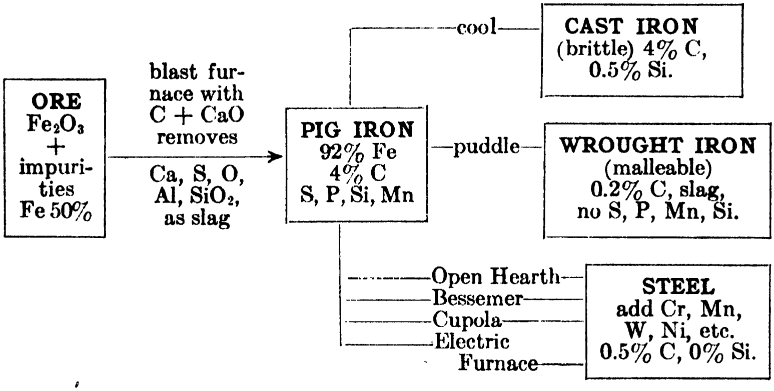


FIG. 140. Metallurgy of Iron.

These processes will be taken up in detail.

### PIG IRON

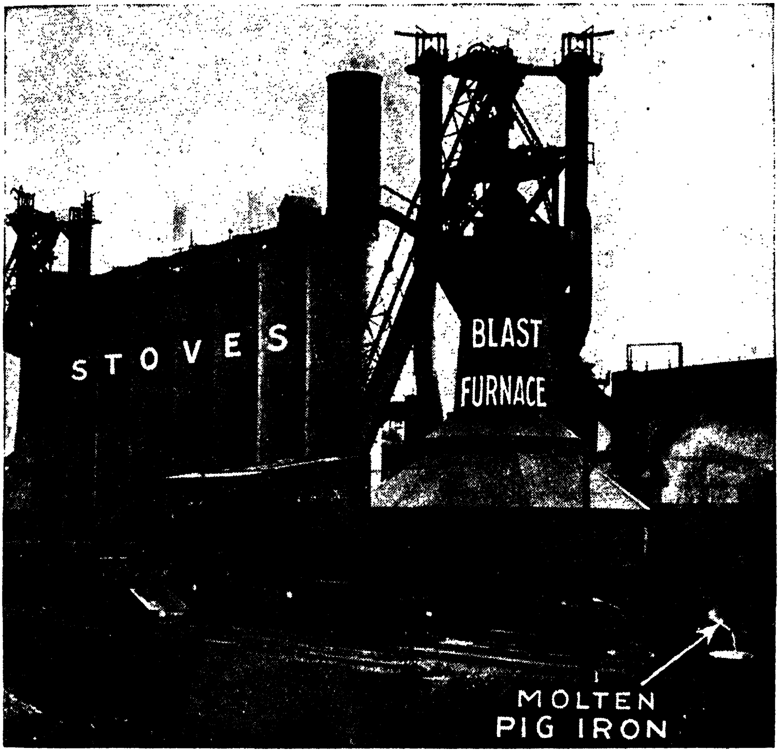
**423. Blast-furnace Pig Iron.**—The iron ore is reduced to pig iron in the **blast furnace** (See Figs. 141, 142). Enormous quantities of raw materials must be fed into the furnace, and the geographical location of blast furnaces is dictated by this. Pittsburgh,

TABLE 89. BLAST FURNACE CHARGE PER TON OF PIG IRON

| | |
|---|---|
| ½ ton Limestone | $CaCO_3 \rightleftarrows CaO + CO_2$ |
| 1 ton Coke (from coal) | $CO_2 + C \rightleftarrows 2CO$ |
| 5 tons Air | $2C + O_2 \rightarrow 2CO$ |
| 2 tons ORE ($Fe_2O_3$ | $Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$ |
| | $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ |
| plus impurities such as $SiO_2$ and $Al_2O_3$ removed as slag) | $SiO_2 + CaO \rightarrow CaSiO_3$ |
| | $Al_2O_3 + CaO \rightarrow Ca(AlO_2)_2$ |

1 TON OF PIG IRON IS PRODUCED.

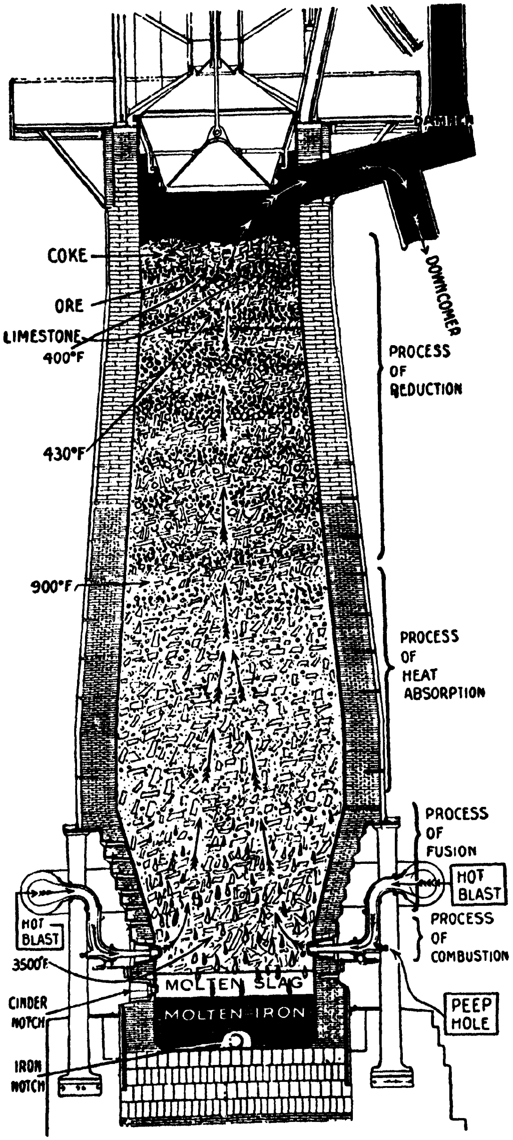
Cleveland, and Detroit are accessible by Great Lake steamers to the shipments of hematite from the Lake Superior region, of coal from Pennsylvania and West Virginia, and of limestone from Michigan.



*Courtesy of the U. S. Steel Corp.*

FIG. 141. The making of pig iron.

The blast furnaces range from 90 to 150 feet in height, and from 12 to 25 feet in diameter (Fig. 142), and produce 500 or more tons of pig iron every 24 hours. The furnace is constructed of heavy steel plates lined with fire-brick. The raw materials are introduced through a bell-shaped hopper at the top of the blast, so manipulated that the furnace gases do not escape. Quantities of air (5 tons for every ton of pig iron produced) are blown in through pipes called **tuyères** (pronounced tweers) near the bottom of the furnace. This air is thoroughly air-conditioned, a single



*Courtesy of the U. S. Steel Corp.*

FIG. 142. Cross-section of the blast furnace.

furnace requiring as large an air-conditioning unit as the whole of Macy's store in New York City. The gases escape out of the pipes (downcomers) near the top of the blast; and usually contain over 20 per cent CO, so that they may be used as a fuel in preheating the air for the blast, or to drive gas engines.

Many reactions occur, but the principle ones are given in Table 89. For example $CO_2$ formed in the lower portion of the blast is reduced to CO by the hot coke higher up in the furnace. CO is particularly effective in reducing the hot **oxides of iron** since CO is a gas and comes into intimate contact with the ore.

The temperature of the upper zone of reduction ranges from 300° to 900°, which is not hot enough to melt the iron. The spongy metal and any remaining oxides descend to the lower zone of reduction where the temperature is 900° to 1,200°. Here, further reduction takes place, the metal then descending to the zone of fusion (1,200° to 1,600°), through which the melting charge trickles down.

**At the bottom of the furnace the products separate into two layers:** the molten iron collects in the bottom, or crucible, of the furnace, while the slag (silicates and aluminates) floats on top of the iron. The two layers are tapped off at the end of each run: the iron is run into sand molds or huge thermos-bottle cars for conveyance to the open hearth, and the slag is taken to the dump. The slag is used for railroad ballast or burned with lime to form a cement; in 1940 Germany began to rework it for its vanadium content.

The world production of iron ore and, from it, pig iron is given in **Table 90** for the year 1937, two years before hostilities began. It is interesting to note the figures for Germany and France, and to speculate on the fate of French iron ore.

TABLE 90. WORLD PRODUCTION OF IRON (1937, gross tons)

| | IRON ORE | PIG IRON |
|---|---|---|
| United States | 73,250,649 | 37,749,575 |
| France | 37,839,000 | 7,916,000 |
| U.S.S.R. | 26,000,000 | 14,520,000 |
| Sweden | 14,952,549 | 692,865 |
| Great Britain | 14,443,146 | 8,629,313 |
| Germany | 9,575,234 | 15,959,806 |
| **Total world production** | **211,000,000** | **104,200,000** |

**424. Properties of Pig Iron.**—The iron which is obtained from the blast furnace is entirely unsatisfactory as a finished product, for in addition to carbon (4 per cent) and silicon (3 per cent) it contains small amounts of phosphorus which make it brittle when cold (cold short) and sulfur which makes it brittle when hot (hot short). These impurities also affect other properties; for instance, pure iron melts at 1535° whereas pig iron melts between 1150° and 1250° depending upon the character of the ore and the operation of the furnace.

### CAST IRON AND WROUGHT IRON

**425. Cupola Cast Iron.**—To make cast iron, pig is melted with scrap iron in a **cupola furnace** (not unlike a small open-hearth), and then run into molds. The carbon (2–4 per cent) in the pig is present as cementite, $Fe_3C$; and if the melt cools quickly a solid solution of the cementite in iron results; this is hard, brittle **white cast iron.** Cooling slowly allows some of the cementite to dissociate into iron and coarse black crystals of graphite, which may be seen in photomicrographs of iron which has been etched away with acid (Fig. 143). Due to the graphite the product has a grey fracture, and is known as **grey cast iron**; it is the better grade of cast iron.

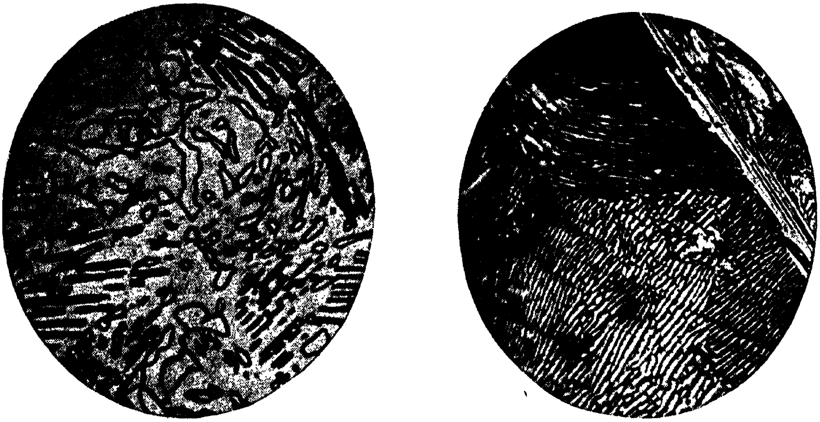


FIG. 143. Photomicrographs of white cast iron (cementite structure, *left*) and grey cast iron (note graphite, *right*). Magnifications × 1700 and × 900.

Both varieties are rigid, but not elastic; and neither can be welded or forged. They are satisfactory, though, for radiators, engine blocks, and any object where strength is not essential. As will be seen in Table 91 the output of cupola cast iron is relatively large.

**426. Wrought Iron.**—Pig iron from which most of the carbon has been removed by blowing air through it (429) is poured into molten slag; and the intimate mixture is cast into ingots. Subsequent rolling and hammering of the ingot produces a soft, fibrous, **wrought iron** in which the slag is distributed throughout fibres of iron. It is malleable, and has great toughness and tensile strength.

In the days of the horseshoe and the blacksmith there was considerable demand for wrought iron; and a pasty mass of slag and pig iron was worked by hand in reverberatory furnace by a **puddler**, who pushed and squeezed and gathered the iron into balls weighing about 100 pounds each, in which form they were worked under a steam hammer.

Despite the inroads which special steels have made, wrought iron is still produced because of its resistance to rust and corrosion. Domestic production in 1939 was 30,606 tons.

## STEEL

**427. General.**—Steel is manufactured from pig iron principally by the **open hearth process** (Table 91). The **Bessemer** and the **electric furnace** processes will also be described. It will be observed that **half of the steel produced in the United States comes from scrap steel, which is added to the furnace along with the pig iron.**

TABLE 91. FURNACES PRODUCING STEEL (U.S.A. 1939)

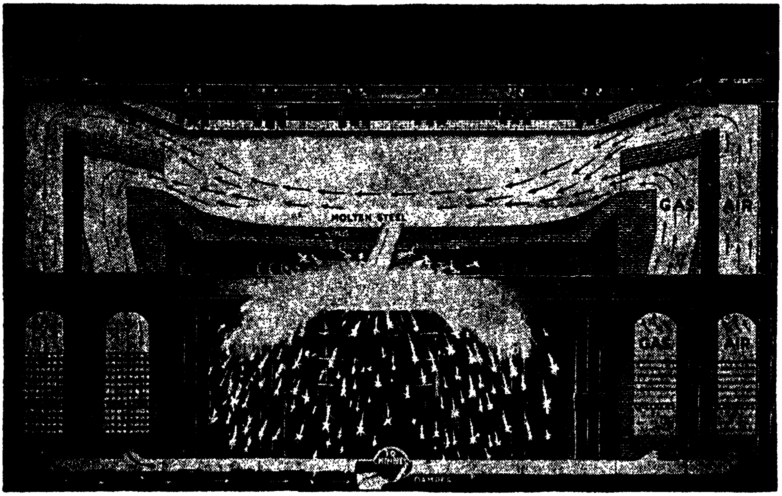
| TYPE OF FURNACE | SCRAP TO STEEL | | PIG IRON TO STEEL | |
|---|---|---|---|---|
| | Gross tons | % | Gross tons | % |
| Open hearth | 22,795,434 | 70 | 23,951,940 | 76 |
| Cupola (cast) | 5,727,405 | 18 | 2,990,355 | 9 |
| Bessemer | 196,544 | 0.6 | 3,217,142 | 10 |
| Electric | 1,493,556 | 5 | 27,270 | 0.1 |
| All others | | 6.4 | | 4.9 |
| **Total** | **32,434,407** | **100%** | **31,457,767** | **100%** |

The open hearth process may be sub-divided:

The Open-Hearth Process (Siemens-Martin) { (*a*) The Basic Open-Hearth Process
(*b*) The Acid Open-Hearth Process

The relative importance of these two processes is indicated for alloy steel in Table 94. The Bessemer process may be similarly sub-divided.

**428. The Basic Open-Hearth Process.**—The basic open-hearth process is employed extensively in the United States for pig irons containing phosphorus. The furnace is lined with a basic material (*e.g.*, magnesite, $MgCO_3$, and recently dolomite $MgCO_3$, $CaCO_3$) which combine with the oxides of phosphorus to form slags.



*Courtesy of the U. S. Steel Corp.*

FIG. 144. Open hearth process of steel making.

The pig iron, scrap steel, and iron ore (*e.g.*, $Fe_2O_3$) are heated on the hearth of a reverberatory furnace. The hearth of the furnace is about 40 feet long, 12 feet wide, and 2 feet deep. Heat is furnished by the combustion of gas or sprayed oil, and it is reflected and radiated upon the charge from the dome of the furnace (Fig. 144).

The temperature of the operation is greatly increased by means of the **Siemens regenerative process.** This means that both the air and gaseous fuel (*e.g.*, producer gas) are preheated by passing through a checkerwork of hot brick. The checkerwork of brick is so placed that the hot products of combustion escaping from the furnace may be conducted through it. While the hot products of combustion are passing through one checkerwork of brick, the

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*Right:* Pouring molten pig iron into an open-hearth furnace. *Courtesy of Youngstown Sheet and Tube Company.*

air and gas are passing through another. By frequently reversing the direction of the gases, it is possible to secure great economy in heating.

The temperature rises to within 30° of the temperature at which the brick lining of the hearth melts: accurate temperature control is therefore imperative. Ordinarily a furnace holds 75 tons and requires 8 hours for an operation. The **carbon** is oxidized to carbon dioxide, which escapes, giving the metal the appearance of boiling. **Silicon, phosphorus,** and **sulfur** are oxidized to anhydrides; these unite with the basic lining (MgO) or flux to form a slag ($MgSiO_3$; $MgPO_3$; $MgSO_4$).

When the proper chemical tests show that the charge has been sufficiently purified, the hearth is tapped and the metal run into ladles, and thence into molds. In this latter operation more or less air is trapped in the liquid, so there is danger of weak places in steel rails or beams unless the gas bubbles are removed. **Deoxidizers or scavengers** are used for this purpose. These substances combine with the absorbed gases, and the resulting compounds pass into the slag.

Manganese, added as spiegeleisen or ferromanganese, is employed extensively; also aluminum, ferrosilicon, vanadium and titanium. A.M.S. metal is an aluminum-manganese-silicon steel said to be very efficient.

The molten metal in the molds forms ingots which, after an important heat treatment in a **soaking pit,** are ready to be rolled and hammered into sheets, rails, bars and girders.

**429. The Acid Bessemer Process.**—This process was patented by an American named Kelly in 1852, but the Englishman Bessemer, visiting Pittsburgh in 1855, bought him out. The acid Bessemer process, employed in the United States, can be applied only to pig irons low in phosphorus and sulfur (why?).

The modern converter is an egg-shaped steel vessel with silica or siliceous refractory material; it revolves on trunnions on its short axis, so that it may be tilted (Fig. 145).

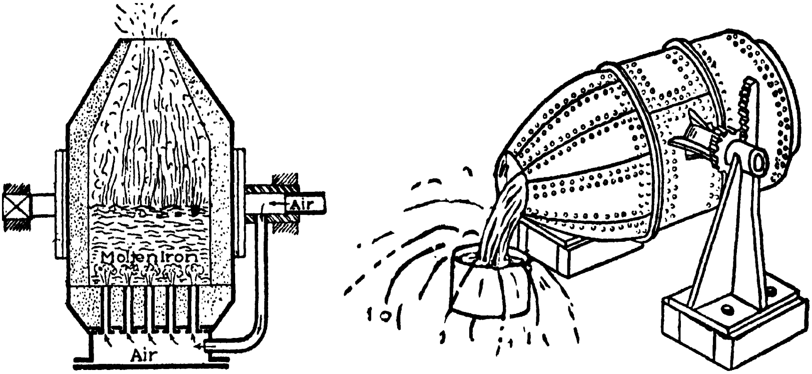
In operating a converter, usually 10 to 20 tons of molten pig iron are poured into the vessel while in the horizontal position; an air-blast is turned on, which enters the bottom of the converter through tuyères; and the vessel is then turned to the vertical position. The air in passing up through the molten metal first **oxidizes iron** to the exclusion of the silicon, manganese, and carbon, FeO being formed:

$$2Fe + O_2 \rightarrow 2FeO.$$

**Silicon and manganese are then oxidized** in turn by the ferrous oxide:

$$2FeO + Si \rightarrow SiO_2 + 2Fe,$$
$$FeO + Mn \rightarrow MnO + Fe.$$

The excess of FeO and the MnO then interact with $SiO_2$ to form slag. The silicon and manganese are therefore oxidized indirectly, much heat being evolved and the metal kept in the liquid state.



THE BLOW. A ten-minute blow oxidizes impurities in the pig iron.

POURING MOLTEN STEEL

FIG. 145. The Bessemer converter.

When the silicon and manganese have been eliminated, the **carbon is oxidized,** and passes off largely as CO, which burns at the mouth of the converter, accompanied by a brilliant shower of sparks (Fig. 145). In the course of 10 minutes nearly all the silicon, manganese, and carbon have been burned out, and the character of the flame indicates that the **blow** is at an end.

The carbon having been completely removed, the converter is turned down, and a carefully **measured quantity of carbon now added;** upon this carbon content the quality of the steel will depend. Usually coke is not used; instead, a high-carbon alloy such as spiegeleisen (4 per cent C, 10 per cent Mn) or ferromanganese (7 per cent C, 80 per cent Mn) is added. The manganese also acts as a deoxidizer or scavenger (428) in removing trapped air from the molten metal.

The **basic Bessemer process** has been largely employed in Germany. The ores of that country contain more phosphorus than do the ores of the United States. The converter is lined with calcined dolomite or limestone, cemented with tar. A phosphate slag is obtained, which has some value as a fertilizer.

**430. Electric-furnace Steel.**—Considerable steel of superior quality is now produced in the **electric furnace,** particularly with scrap steel as the raw material (Table 94). As the operation is carried out at very high temperatures, the impurities are more completely removed, especially gases. Phosphorus and sulfur are almost completely eliminated, and deoxidation is more complete than that attained by other processes.

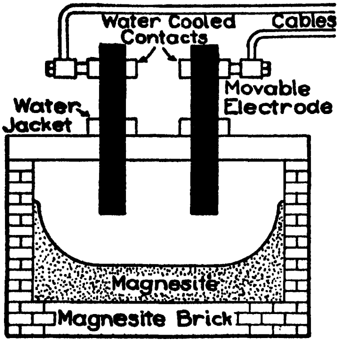


FIG. 146. Heroult electric furnace.

It is somewhat similar to the open-hearth process, but heat is generated by electricity (Fig. 146, Heroult type furnace) instead of by hot gases. Although the charge is small—about 20 tons—heats can be made hourly; so that the furnace may rival the total capacity of a 100-ton open-hearth making two heats a day. During the process, other metals such as chromium, nickel and tungsten may be added. A homogeneous steel free from dirt and slag is obtained; it is especially suitable for razors, tools, cutlery, needles, files, and so forth.

Formerly these special steels were made by heating very pure open-hearth or wrought iron with charcoal in a *crucible* of clay and graphite. Only 1745 tons of crucible steel was made domestically in 1939.

**431. Composition of Steel.**—

TABLE 92. QUANTITATIVE ANALYSES OF STEELS

| | Pig Iron | Acid Bessemer Steel | Basic Open-Hearth Steel |
|---|---|---|---|
| Iron, Fe | 93.32% | 98.372% | 99.155% |
| Carbon, C | 3.5 | 0.460 | 0.366 |
| Silicon, Si | 2.0 | 0.087 | 0.012 |
| Manganese, Mn | 1.0 | 0.910 | 0.419 |
| Phosphorus, P | 0.10 | 0.102 | 0.012 |
| Sulfur, S | 0.08 | 0.069 | 0.036 |

These analyses were made by the Bureau of Standards at Washington. The percentage of iron was obtained by difference.

In discovering the differences between pig iron and steel, examine the table and answer the following questions. What two elements have had their percentages considerably reduced? What effect has the *acid* Bessemer process upon P? upon S? upon Mn? Compare this with the effect of the *basic* open hearth, and explain.

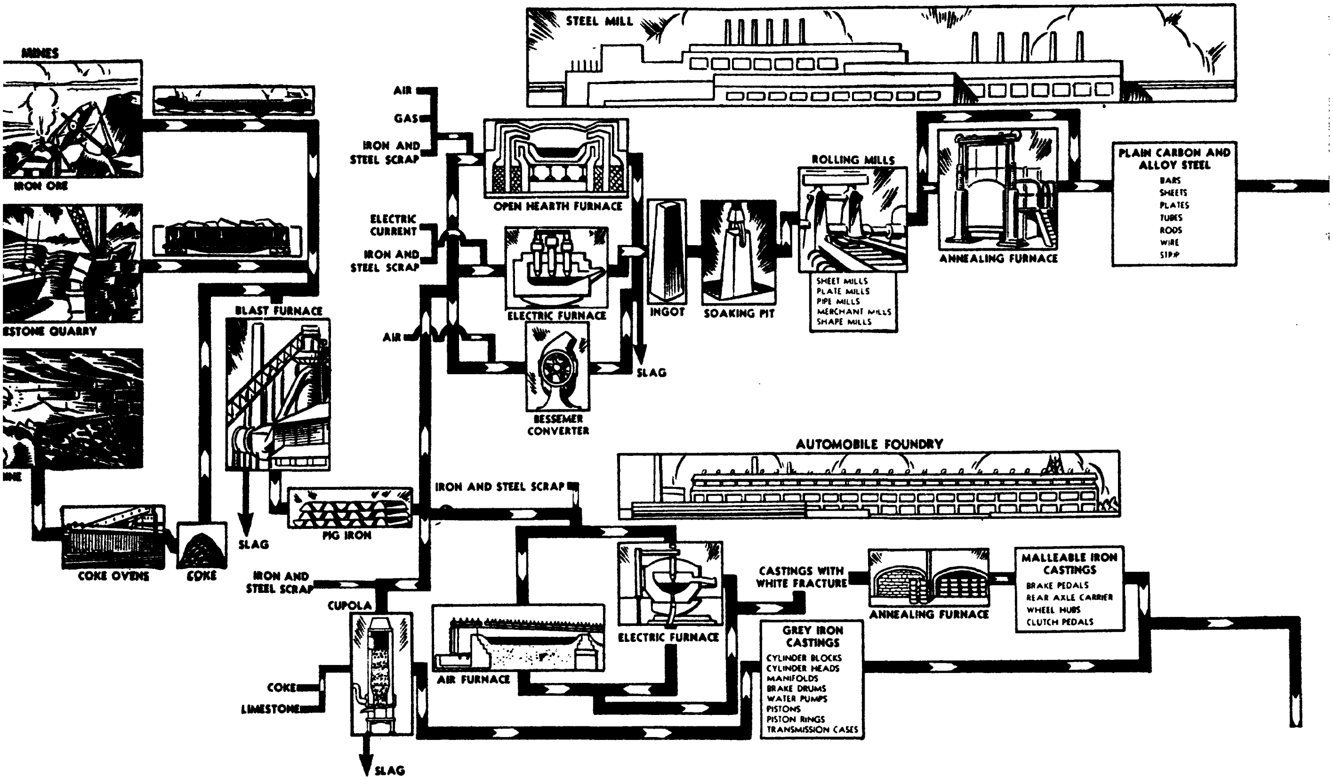
**432. The Hardening of Steel.**—**Low carbon steels** (under 0.5 per cent) are soft, and ductile; but **high carbon steels** (0.5 to 2 per cent) are hard and brittle. A soft or wrought-iron steel may be **case-hardened** by heating it in powdered carbon: a thin layer of iron is converted into hard high-carbon steel on the body of the softer metal. Processes similar to this are employed for case-hardening automobile gears and armor plate.

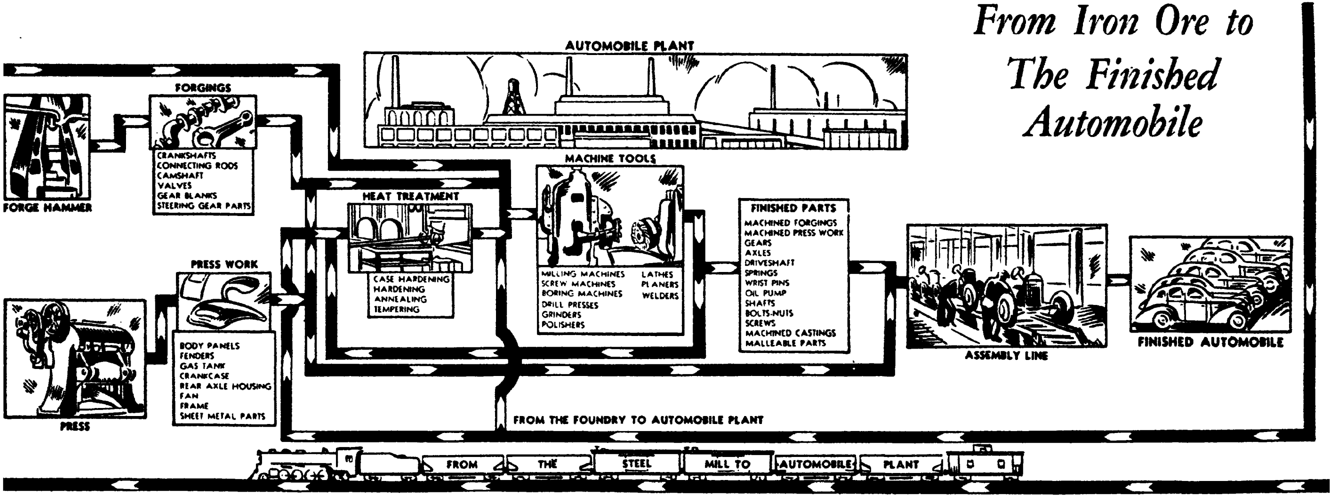
If a high-carbon steel is heated to a high temperature and suddenly chilled by plunging into water or oil, it becomes exceedingly hard and brittle.

**433. The Tempering of Steel.**—If the temperature-hardened high-carbon steel in the foregoing paragraph is reheated to 220–320° and slowly cooled, it becomes softer and less brittle. This is called **tempering** the steel. 230° gives the hardest temper. By regulating the hardening and tempering processes, a steel of practically any desired hardness may be obtained. This was the principle which produced the superb Damascus and Toledo steels of old; and which today makes steel for razors, surgical instruments and springs.

*Courtesy of General Motors Corp.*

FIG. 147. Photomicrographs.


MINES
IRON ORE
ESTONE QUARRY
INE
COKE OVENS
COKE
BLAST FURNACE
SLAG
PIG IRON
AIR
GAS
IRON AND STEEL SCRAP
ELECTRIC CURRENT
IRON AND STEEL SCRAP
AIR
STEEL MILL
OPEN HEARTH FURNACE
ELECTRIC FURNACE
BESSEMER CONVERTER
SLAG
INGOT
SOAKING PIT
ROLLING MILLS
SHEET MILLS
PLATE MILLS
PIPE MILLS
MERCHANT MILLS
SHAPE MILLS
ANNEALING FURNACE
PLAIN CARBON AND ALLOY STEEL
BARS
SHEETS
PLATES
TUBES
RODS
WIRE
STRIP
IRON AND STEEL SCRAP
AUTOMOBILE FOUNDRY
IRON AND STEEL SCRAP
CUPOLA
COKE
LIMESTONE
SLAG
AIR FURNACE
ELECTRIC FURNACE
CASTINGS WITH WHITE FRACTURE
ANNEALING FURNACE
MALLEABLE IRON CASTINGS
BRAKE PEDALS
REAR AXLE CARRIER
WHEEL HUBS
CLUTCH PEDALS
GREY IRON CASTINGS
CYLINDER BLOCKS
CYLINDER HEADS
MANIFOLDS
BRAKE DRUMS
WATER PUMPS
PISTONS
PISTON RINGS
TRANSMISSION CASES



*Courtesy of General Motors Corpora*

148. From iron ore to the finished automobile. Questions pertaining to the above diagram. *Raw materials:* Which States furnish iron ore? limestc not the coal transported to the iron fields instead? *Pig iron:* What are the two products of the blast furnace? What other raw material, wl to the furnace in tonnage lots, is not shown in the diagram? To what two general plants is the pig sent? *Steel mill:* What relative percentage treated by the above three processes? (The ingot is soaked to give it an even temperature for rolling.) *Foundry:* What is added to the pig in r? Photomicrographs reveal what differences between grey and white castings? *Automobile plant:* What three treatments are given steel? Wha t treatment given to castings in the automobile plant? Which of the following are case-hardened before making the finished parts: gears, pist ission cases, wheel hubs, screws, malleable parts, springs, gas tank, fenders?

These properties of steel can be explained simply in terms of its molecular structure. Low-carbon steel is a pure, **soft** form of iron known as **ferrite.** Now high-carbon steel contains **cementite,** $Fe_3C$, as we saw in the section on cast iron (**425**). If the high-carbon steel is quickly chilled, the cementite (which normally precipitates out of ferrite) forms a supersaturated solution of **cementite in ferrite.** That is, the cementite intrudes into the ferrite lattice, holding the ferrite crystals rigid: the ferrite is no longer soft. Reheating (*tempering*) permits some of the supersaturated cementite to crystallize out; this gives a lattice of pure ferrite (soft) interspersed with separate crystals of cementite.

**434. Photomicrography.**—The microscope and photography have become very important in the study of the structure of metals and alloys. When the surface of iron or of steel is polished and then carefully etched by means of acids, something may be learned about the characteristic crystalline formations. **Photomicrographs** (Fig. 147) are made, and the relation of crystalline forms to physical properties may be studied. This branch of science is called **metallography.**

**435. Alloy Steels.**—Carbon is the most important element known for controlling the properties of the final steel. However, **heat-treatment is facilitated when certain metals (Ni, Cr, V, W, Mo, etc.) are added to the melt.** This is the basis of our modern alloy-steel civilization, where huge masses of steel must be skill-

TABLE 93. PROPERTIES AND USES OF ALLOY STEELS

| ELEMENT | PROPERTIES (all increase hardness) | USES AND COMPOSITION |
|---|---|---|
| Chromium<br>Cr-V same | resist corrosion | stainless steel (18%); tools, armor (12–15%). |
| Manganese | tough | machine tools (1–7%); rock-crushers, safes (7%). |
| Nickel | tenacity | structural (0.5%); armor plate (3–5%). |
| Silicon | acid-resisting | Duriron vessels (15%). |
| Tungsten, Mo,<br>Co same | retain temper at high temperatures | high-speed lathe cutting-tools, scalpels. |

fully tempered, as for example in modern heavy artillery. Consider the specifications for an 18-inch calibre Naval gun weighing 150 tons: it must hurl a projectile weighing 3000 pounds 30 miles. If the target is near, the projectile will pierce 40 inches of steel plate; at 30 miles it will pierce a foot of solid plate: yet such a missile has the momentum of an 8-car express train going 60 miles an hour.

Table 94 indicates the quantity of special alloy steels made in the United States. The figure 2,867,817 tons should be compared with the total domestic steel production of 51,721,369 tons.

TABLE 94. ALLOY STEEL PRODUCTION (U.S.A., 1939; gross tons)

| ALLOYS FOR SPECIAL STEELS | | FURNACES MAKING STEEL FROM THESE ALLOYS | |
|---|---|---|---|
| Ferromanganese | 296,631 | Open hearth | |
| Spiegeleisen | 84,739 | basic | 2,055,601 |
| Ferrosilicon | 343,922 | acid | 139,804 |
| Ferrophosphorus | 13,320 | Electric | 669,093 |
| Ferrotungsten | 1,609 | Bessemer | 3,113 |
| Other varieties | 101,041 | Others | 206 |
| **Total** | **841,162** | **total** | **2,867,817** |

## QUESTION REVIEW

I. GENERAL. **Historical** (420). **Occurrence** (421). **Metallurgy** (422).

1. What is the most important iron ore? Where is it located? Is any of it mined from underground? What is meant by blood-count?
2. Draw a flow-sheet showing from iron ore to finished product.

II. PIG IRON. **Blast furnace pig-iron** (423). **Properties** (424).

3. How is each of the following involved in making pig-iron: coke, lime, limestone, air, hematite, aluminum silicate, slag, tuyères, Pittsburgh, West Virginia, Michigan, downcomers, ballast, cold short?
4. What countries are the chief world producers of iron ore? of pig iron?
5. What effect does sulfur have on iron? What effect does phosphorus have on iron?

III. CAST AND WROUGHT IRON (425–6).

6. Distinguish between the molecular constitution of white cast iron, wrought iron, and grey cast iron. How are these structures revealed?
7. What is a cupola, photomicrograph, puddler, ingot?

IV. STEEL.

**a. General** (427).

8. What two processes are the chief consumers of steel scrap? of pig iron?
9. What is meant by the "basic" and "acid" processes?

**b. The basic open hearth process** (428).

10. Describe the Siemens regenerative process.
11. Give equations showing how carbon and phosphorus are removed. What are deoxidizers?

**c. The acid Bessemer process** (429).

12. Describe each step involved in the Bessemer process. Why does Germany use the basic Bessemer process?

**d. Electric furnace steel** (430).

13. What advantage has this method over the open hearth? What method has it displaced?

**e. Composition of steel (431).**

14. Answer the questions in section 431.

V. ALLOY STEELS.

**a. The hardening of steel (432). Tempering (433).**

15. Show that case hardening illustrates the effect of carbon on the physical properties of steel. How else may steel be hardened?
16. Contrast the molecular composition of a tempered steel with that of a soft steel.

**b. Photomicrography (434).**

**c. Alloy steels (435).**

17. What general advantage is gained by alloying metals with steel?
18. What do the following metals contribute to alloy steel: nickel, manganese, tungsten, silicon, chromium?

**Reading References:** Articles number 11, 30, 40, 102, 107, 130, 137, 141 and 228 in the Appendix.

# CHAPTER XXXII

## GROUP VIII. THE IRON GROUP. THE PLATINUM METALS

**436. Relationships.**—Group VIII of the periodic system contains three triads of metals. The first of the triads is the iron family: iron, cobalt and nickel. These are among the "transition elements," in which the third state is being completed; the $4s^2$ is common to them all, which accounts for a similarity of properties. Cobalt and nickel resemble one another more closely than they do iron; for iron is more like chromium and manganese, the two elements which precede iron in the periodic table.

TABLE 95. THE IRON GROUP

| Element | Atomic Weight | Atomic Number | Arrangement of Planetary Electrons | Density | Melting Point | Boiling Point |
|---|---|---|---|---|---|---|
| Iron (*ferrum*), Fe | 55.85 | 26 | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$ | 7.86 | 1535° | 3000° |
| Cobalt, Co | 58.94 | 27 | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$ | 8.9 | 1480° | 2900° |
| Nickel, Ni | 58.69 | 28 | $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$ | 8.9 | 1452° | 2900° |

The elements are difficult to melt, iron being the least fusible and nickel the most fusible. The metals are magnetic, iron showing this property most strongly. Iron forms the most stable oxides and chlorides, and nickel the least stable. Thus, $FeCl_3$ can be volatilized without decomposition, whereas $CoCl_3$ is very unstable, and $NiCl_3$ is unknown. The valences exhibited are: $Fe^{++}$, $Fe^{+++}$, $Co^{++}$, $Co^{+++}$, and $Ni^{++}$. Notice that nickel forms nickelous salts only. Of these the most stable salts are: ferric, cobaltous, nickelous. Many of the salts are deliquescent. All the metals occlude hydrogen, nickel being superior in this respect. In the finely divided state they are employed as catalysts. Thus, nickel is used in the hydrogenation of fats and unsaturated hydrocarbons. Iron rusts when exposed to moist air, but cobalt and nickel undergo oxidation only when heated in air. All these metals form **carbonyls** of the type $M(CO)_4$, and have a great tendency to form complex ions (**323**).

The second and third group of triads, the platinum metals, are so similar in properties that they will be considered together (447–457).

### IRON $^{55.85}_{26}\text{Fe}$

**437. Properties.**—The metallurgy of iron has been taken up in the preceding chapter.

Pure iron possesses a silver-white luster; it has a density of 7.86 and melts at 1,535°. Iron is attracted by the magnet; it may also be rendered magnetic, but it loses its magnetism readily. Iron, unlike steel, cannot be hardened by sudden cooling, and is therefore of much less value. The pure metal may be obtained by reducing pure oxides of iron by hydrogen, or by the electrolysis of a boiling solution of ferrous sulfate ($FeSO_4$) between iron electrodes, which yields a product containing 99.98 per cent of iron.

Chemically, iron is a fairly active metal, standing just below zinc. Thus, it displaces hydrogen readily from dilute acids. Pure iron rusts very slowly in pure water at ordinary temperatures. With water containing carbon dioxide in solution, the rate of corrosion is greatly increased.

#### DEMONSTRATION 119. PASSIVE IRON

Materials: Four beakers containing fuming nitric acid, distilled water, dilute nitric acid, copper sulfate; two 2 × 6″ sheets of iron, file, hammer.

A peculiar state known as **passive iron** is made by dipping iron sheet into fuming nitric acid, and then rinsing in distilled water. The surface is changed in a manner not well understood. Such passive iron is chemically inert and may be dipped into dilute or concentrated nitric acid, or copper sulfate, without being attacked. Upon being scratched or struck a sharp blow, however, it loses its passivity, and immediately reacts with these solutions.

**438. Iron Compounds.**—Iron forms ferrous, $Fe^{++}$, and ferric, $Fe^{+++}$, compounds; of these the latter are more stable.

**Ferrous hydroxide,** $Fe(OH)_2$, may be obtained as a white flocculent precipitate by treating a solution of a ferrous salt with an alkali, oxygen being excluded; it readily absorbs oxygen, turning dark green, and finally forming reddish-brown ferric hydroxide, $Fe(OH)_3$.

**Ferrous sulfate,** $FeSO_4, 7H_2O$, is often called **green vitriol,** or **copperas.** This salt may be obtained by dissolving iron in dilute sulfuric acid, with the exclusion of oxygen, and by concentrating the solution until crystallization occurs. It is also manufactured by the oxidation of iron pyrites:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4.$$

The salt is used in the purification of water, in the dyeing industry, as a reagent for killing weeds, and in black inks.

**Ferric hydroxide,** $Fe(OH)_3$ is a brown precipitate identical with iron rust, which occurs as the mineral limonite. Upon heating, it loses water and forms ferric oxide, $Fe_2O_3$, (hematite). This latter is the pigment Venetian red used for farm buildings, roofs, railway cars, etc.

**439. Inks and Blue Prints.—Black ink** contains ferrous sulfate and tannins (nut-galls, which are 50–60 per cent tannins); this forms colorless ferrous tannate, which oxidizes to form black ferric tannate when the ink is used. Black dye is added to the ink to make it black originally. Black ink spots, and this applies to rust spots as well, may be removed by soaking in ammonium oxalate solution so as to form soluble ferric oxalate.

Inks were prepared from iron salt and nut-galls many centuries ago, and were undoubtedly used by early authors in writing on parchment. In case such writing has become illegible, due to the fading of the ink, it may be restored by treating the manuscript with a dilute solution of ammonium sulfide. The writer treated a very valuable manuscript of the fourteenth century in this way, and obtained remarkable effects.

**Blue prints** utilize the principle that light reduces ferric salts (oxalate, citrate) to ferrous salts; and that subsequent treatment of the salts with potassium ferricyanide, $K_3Fe(CN)_6$, forms Turnbull's blue with the ferrous salts but does not affect the ferric salts.

Commercial blue-print paper is often coated with a mixture of ferric ammonium citrate (or ferric ammonium oxalate) and potassium ferricyanide. A transparent drawing or negative is placed over the paper, and the whole exposed to strong light; light reduces ferric salts to the ferrous condition. The paper is then dipped in water; this forms Turnbull's blue with the ferrous salt:

$$\text{Photoreduction: } Fe^{+++}\text{Citrate} \xrightarrow{\text{light}} Fe^{++}\text{Citrate}.$$

$$\text{Development: } 3Fe^{++} + \underset{\substack{\text{ferricyanide}\\ \text{developer}}}{2(Fe(CN)_6)^{\equiv}} \rightarrow \underset{\substack{\text{ferrous ferricyanide}\\ \text{Turnbull's blue}}}{Fe_3(Fe(CN)_6)_2}.$$

The potassium ferricyanide forms Turnbull's blue with the photochemically reduced ($Fe^{++}$) portions of the paper, leaving a blue print on a white background; while the ferric salts which were not reduced are washed away.

### DEMONSTRATION 120. BLUE PRINTING

**Materials:** Three test-tubes, solutions of ferrous oxalate, ferric nitrate, potassium ferricyanide, blue-print paper, strong light, a negative or transparent line drawing.

Potassium ferricyanide is added to (*a*) ferrous oxalate, (*b*) ferrous oxalate exposed to light, (*c*) ferric nitrate. Turnbull's blue is obtained only in (*b*). A blue-print of the line drawing is also made.

Another complex cyanide, used as a pigment and for bluing in the laundry, is **Prussian blue,** ferric ferrocyanide. This is formed by mixing a ferric salt with potassium ferrocyanide:

$$4Fe^{+++} + 3(Fe(CN)_6)^{-4} \rightarrow \underset{\substack{\text{ferric ferrocyanide} \\ \text{Prussian blue}}}{Fe_4(Fe(CN)_6)_3}.$$

Neither potassium ferrocyanide (yellow) nor potassium ferricyanide (red) are poisonous, although potassium cyanide, KCN, is a deadly poison.

### COBALT ${}^{58.94}_{27}Co$

**440. Metallurgy.**—**Cobalt** (German *Kobold*, goblin) was discovered by the Swedish chemist Brandt, in 1735, who stated that the blue color of smalt depends upon the presence of this metal.

Cobalt usually occurs in combination with arsenic and sulfur in complex minerals also containing iron, nickel and copper, *e.g.*,

| | |
|---|---|
| Smaltite (cobalt arsenide) | CoAs |
| Cobaltite (cobalt-arsenide-sulfide) | CoAsS |

Although at one time the nickel-cobalt-arsenide deposit at Cobalt, Canada, was the chief source of cobalt, lately the Belgian Congo and Northern Rhodesia have become most important: the latter produced 3581 tons in 1939 compared with 332 tons from Ontario. The United States is not a producer.

Metallic cobalt is obtained by smelting, not unlike the treatment of nickel. Electric furnaces are often used. It may also be made by heating the oxide in a current of hydrogen or carbon monoxide, or by reduction with aluminum or carbon.

**441. Uses of Cobalt.**—Cobalt resembles nickel more closely than it does iron. **Stellite,** invented by Haynes of automobile fame, is an alloy of cobalt, chromium and tungsten; and it is used in manufacturing lathe tools and surgeons' and dentists' knives. The cutting edge is not dulled at red heat, so that army surgeons can sterilize their scalpels by holding them in a flame. Other uses for cobalt include electroplating, hardening steel, permanent magnets, and carboloy (419). See table 93, section 435.

Extensive research has found continued outlets for cobalt: cobalt oxide in the ceramic industry, organic cobalt salts as driers in the paint industry; cobalt metal in high-speed tool steels and magnetic alloys, and cobalt oxides as hydrogenation catalysts.

**442. Compounds of Cobalt.**—Cobalt forms both cobaltous, $Co^{++}$, and cobaltic, $Co^{+++}$, compounds; the cobaltous salts are the more stable.

### DEMONSTRATION 121. COBALT COMPOUNDS

Materials: Large test-tube, solid $CoCl_2, 6H_2O$ and KCNS, ether, solution of $AgNO_3$, pen and paper, burner.

Cobaltous compounds are generally pink, while the anhydrous salts are blue. If solid cobaltous chloride and potassium thiocyanate are shaken together in a tube, a blue cobaltous compound, $K_2Co(CNS)_4$ is formed which dissolves in ether without ionizing. If, now, water is added, some of the cobaltous ion appears as a pink aqueous layer. The contents of the tube can be made patriotic (pink, white and blue) by adding silver nitrate (what forms?).

This principle is applied popularly in "weather indicators" which turn from blue to pink upon the approach of wet weather. Writing with an aqueous solution of a cobaltous salt is practically colorless (pale pink); heating expels water and the writing becomes visible (blue).

Cobaltic salts form stable coordinate-covalent bonds (**323**), giving rise to a variety of complex compounds. These were carefully investigated by Werner a half-century ago. Most of them are brightly colored, and show interesting properties. For example, upon the addition of silver ion to the first of the following compounds only AgCl will precipitate, whereas with the second compound only AgBr will be obtained; *i.e.*, the chlorine within the bracket is too tightly bound by covalence to give a precipitate (compare the Cl in $KClO_3$).

| | |
|---|---|
| Bromo-pentammine-cobalti-chloride | $[Co^{+3}Br^{-1}(NH_3)_5{}^0]^{+2}Cl_2$ |
| Chloro-diaquo-triammino-cobalti-bromide | $[CoCl(H_2O)_2(NH_3)_3]Br_2$ |
| Sodium nitro-tribromo-hydroxy-ammino-cobaltate | $Na_2[Co^{+3}(NO_2)^{-1}Br_3{}^{-1}(OH)^{-1}(NH_3)^0]^{-2}$ |
| Potassium cobalti-nitrite or potassium hexanitro-cobaltate | $K_3[Co(NO_2)_6]$ |

With the exception of the last compound, these particular complex salts have no special importance; they merely illustrate how great a variety of complex salts may be formed. It will be noticed that the complex cobalt ion always has six radicals about it. Also, notice the valences within each complex. The potassium cobalti-nitrite is obtained whenever a cobaltous salt, a salt of potassium, and a nitrite are mixed. This is useful in analysis for either potassium or cobalt, serving to distinguish these elements from sodium and nickel which do not form precipitates under similar conditions. It is also used as a pigment.

### NICKEL $^{58.69}_{28}Ni$

**443. Metallurgy.**—**Nickel** was discovered by the mineralogist Cronstedt in 1751. It is usually associated with cobalt; and 80 to 90 per cent of world production comes from the ore

**Pentlandite**. . . . (Ni, Co, Fe, Cu)S

from the International Nickel Co. at Sudbury, Ontario. The other source is the hydrated nickel-magnesium silicates of New Caledonia. World production in 1938 was 127,000 short tons of nickel, and only 2,000 tons of reclaimed nickel. The metallurgy of the element is complicated, the method adopted depending upon the nature of the ore. For the sulfide ores of Canada, the treatment is as follows:

(a) The ore is first heap-roasted to oxidize iron and sulfur.

(b) The roasted ore is then smelted in a blast furnace to produce a matte (36 to 40 per cent Ni + Cu).

(c) This matte is then bessemerized to a matte containing about 80 per cent of Ni + Cu and nearly 20 per cent of S.

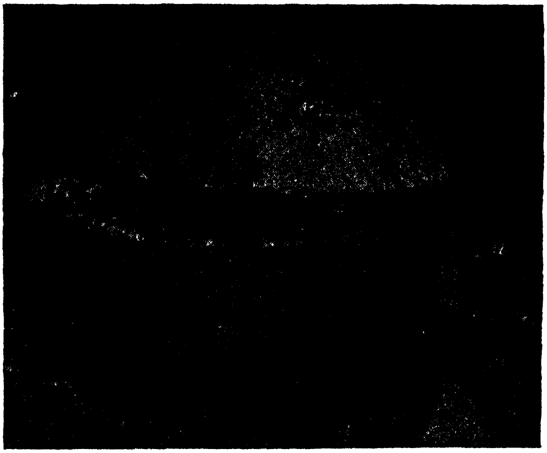
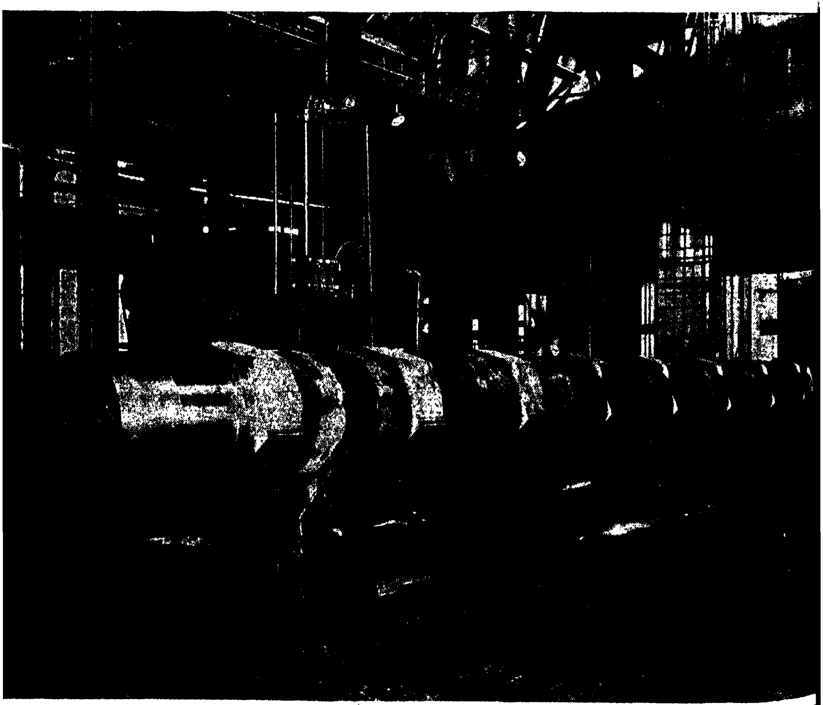


FIG. 149. Orford process for separating nickel and copper. After chemical action of sodium sulfate on copper-nickel sulfide in the presence of carbon fracture takes place into a copper-soda top and a nickel bottom.

(d) There are different processes for producing nickel from the Ni-Cu matte. In the **Mond process,** the metal is converted into nickel carbonyl $Ni(CO)_4$, which decomposes at about 200° C., yielding nickel. Nickel and copper may also be separated by electrolysis.

**444. Uses of Nickel.**—Nickel is a whitish metal with a tinge of yellow. It has a density of 8.9, melts at 1,452°, and is malleable, ductile, and magnetic. The metal rusts slowly in moist air, and is very resistant to the attack of hot alkalies; it is difficult to oxidize, displaces hydrogen with difficulty, but dissolves in nitric acid to form the nitrate.

Among nickel alloys, **Monel metal** is characterized by its resistance to acid corrosion. It is a 60–72 per cent Ni alloy containing Cu and small amounts of Fe and Mn; and it is produced directly from the Ni-Cu matte of the Sudbury ores. **Invar** has an



*Courtesy of Bethlehem Steel C*

FIG. 150. Hollow forged nickel steel shaft.

exceedingly low coefficient of thermal expansion; and so it is valuable for pendulum rods, surveyor's tapes, and meter-scales. **Nichrome** (Ni-Cr-Fe-Mn) withstands high temperatures without corrosion, and since it has a high electrical resistance it is used for domestic electrical appliances. **Permalloy,** containing 80 per cent nickel and 20 per cent iron, possesses the remarkable magnetic property of being easily magnetized by feeble currents.

For electroplating nickel a bath of pure ammonium nickel sulfate, $(NH_4)_2SO_4$, $NiSO_4$, $6H_2O$ is used.

**445. Nickelous Compounds.**—Nickel forms only one series of salts, the nickelous: *e.g.*, $NiCl_2$; $NiSO_4$; $Ni(NO_3)_2$; etc. $Ni^{++}$ in solution or crystals is green; anhydrous salts are usually yellow. The sulfide, carbonate, hydroxide and phosphate are insoluble in water. The sulfate, $NiSO_4$, $6H_2O$ and the ammonium sulfate are the most common soluble salts of the metal.

**Nickel carbonyl,** $Ni(CO)_4$, is a colorless liquid, which boils at about 43°. The compound is decomposed by heat, being explosive at 60°. The vapor is highly poisonous. One method for the preparation of nickel is based upon heating this compound.

**446. Analysis of the Iron Family.**—Borax bead tests show iron, green; cobalt, a fine blue; nickel, brown in the oxidizing flame, grey in the reducing flame.

Ferrous compounds precipitate light Turnbull's blue with potassium ferricyanide, whereas ferric compounds give dark Prussian blue with potassium ferrocyanide. With potassium thiocyanate, KCNS, ferrous compounds give no coloration; with ferric compounds a blood-red color (211) is obtained. This is an extremely sensitive test for iron.

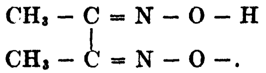
### DEMONSTRATION 122. ANALYSIS OF THE IRON FAMILY

Materials: Ten test glasses, solutions of $Fe^{++}$, $Fe^{+++}$, $Co^{++}$, $Ni^{++}$, $NH_4OH$, potassium ferricyanide, potassium ferrocyanide, dimethylglyoxime, KCNS.

In **routine qualitative analysis** the three metals are precipitated in Group III with ammonium sulfide. In solution, $Fe^{+++}$, $Co^{++}$ and $Ni^{++}$ are separated with $NH_4OH$, which forms insoluble $Fe(OH)_3$ and soluble complex-ammines of cobalt and nickel. The iron is later identified by forming Prussian blue. The ammoniacal solution of nickel is treated with dimethylglyoxime, with which it gives a brilliant scarlet precipitate; cobalt does not give this reaction.

$$Ni(OH)_2 + \underset{\text{dimethyl-glyoxime}}{2X \cdots H} \rightarrow 2H_2O + \underset{\text{scarlet precipitate}}{X \cdots Ni \cdots X}$$

in which X is



$$\begin{array}{l} CH_3 - C = N - O - H \\ \qquad\quad | \\ CH_3 - C = N - O - . \end{array}$$

**Cobalt** is identified by forming blue $K_2Co(CNS)_4$ in a layer of ether (442), or the insoluble $K_3Co(NO_2)_6$ (442).

## THE PLATINUM FAMILY

**447. General Characteristics.**—The second and third group of triads in Group VIII are known as the precious metals of the platinum family. Their properties are given in Table 96.

TABLE 96. THE PLATINUM FAMILY

| Element | Atomic Weight | Atomic Number | Density | Melting Point | Boiling Point |
|---|---|---|---|---|---|
| Ruthenium, Ru | 101.7 | 44 | 12.2 | 2450° | 4150° |
| Rhodium, Rh | 102.91 | 45 | 12.5 | 1985° | >2500° |
| Palladium, Pd | 106.7 | 46 | 11.4 | 1555° | 2200° |
| Osmium, Os | 190.2 | 76 | 22.5 | 2700° | 4450° |
| Iridium, Ir | 193.1 | 77 | 22.4 | 2440° | 4400° |
| Platinum, Pt | 195.23 | 78 | 21.45 | 1755° | 4050° |

Platinum and its allied metals are greyish white, heavy, difficultly fusible, possess little reactivity and therefore offer great resistance to corrosion. Owing to their lack of activity, they are easily separated from their compounds and are found in nature in the free state.

Like cobalt and nickel, the members of the platinum family tend to form complex ions, such as $PtCl_6^=$ and $OsO_6^=$. They have a multiple valence.

**448. Occurrence.**—Platinum and its allied metals are found together in the free state in the Ural mountains of Russia, usually in gravels; and as **sperrylite,** $PtAs_2$ in the nickel ores at Sudbury, Canada. Analysis of the precious-metal sediments in Alaskan creeks is given as:

Pt 60–74 per cent; Ir 6–22 per cent; Os 0.7–4 per cent; Ru 0.1–0.4 per cent; Rh 0.4–1.9 per cent; Pd 0.2–0.6 per cent; gold 0.3–2.2 per cent; other impurities 11–18 per cent.

Although at one time Russia was chief producer, Canada has so improved the recovery of these metals during the refining of its Sudbury nickel ore, that 57 per cent of the world production in 1938 was obtained in that fashion, as contrasted with 17 per cent in 1929. World trends are shown in Fig. 152.

**449. Uses.**—The metals of the platinum family which are of industrial importance are platinum, palladium and iridium.

Of the **platinum** consumed domestically in 1939, 57 per cent was by jewelers as a setting for precious stones; 20 per cent by chemists for acid resistant ware, and as catalysts for the sulfuric acid process and for organic hydrogenations; 14 per cent by the dental industry for bridges and bracings; and 12 per cent for electrical appliances such as thermocouples, furnace windings, contact-points and so forth. Platinum leaf for outdoor signs made its appearance in 1939; palladium leaf has been in use since 1933.

*Courtesy of Baker and Co.*

FIG. 151. Platinum nugget, South America, 1896. Weight 20.4 ounces. Photograph one-half actual size.

**Palladium** is the second most extensively used precious metal of the platinum family. Less costly than platinum, although less abundant, it is alloyed with or substituted for platinum chiefly in the dental and electrical industries.

A per cent or two of **iridium** is added to platinum to stiffen it, especially for chemical ware.

The remaining three elements constituted only 1.5 per cent of the total group-consumption in 1939. **Rhodium** is alloyed with platinum for resistance wire and laboratory ware; it is used in searchlight reflectors and also, in 1939, as an improvement over gold-platinum spinnerets (655) in the rayon industry. **Osmium** tips keep gold pen-points from corroding. The oxide is a biological stain for fats and fingerprint work. **Ruthenium** is added in hardening platinum alloys, and also is used in a biological stain.

The domestic consumption and prices for these precious metals are given in Table 97. Although the United States is only fourth-ranking producer it is by far the largest consumer.

TABLE 97. PLATINUM METAL STATISTICS

| | U. S. CONSUMPTION 1939, troy oz. | U. S. PRICES 1930 (per oz.) | U. S. PRICES 1939 (per oz.) |
|---|---|---|---|
| Platinum | 100,266 | $62 | $32 |
| Palladium | 51,406 | 24 | 22 |
| Iridium | 4,322 | 250 | 110 |
| Osmium | .... | 70 | 36 |
| Rhodium | 2,363 | 53 | 120 |
| Ruthenium | .... | 41 | 50 |

### PLATINUM $^{195.23}_{78}\text{Pt}$

**450. History and Preparation.—Platinum** (Spanish *platina*, dim. of *plata*, the Spanish for silver) appears to have been observed in the sixteenth century;

**but it did not attract general attention until the eighteenth century. About 1750 it was examined by Watson, by Brownrigg, and by Scheffer, being termed by the last "white gold," or "platina del Pinto," *i.e.*, small silver of Pinto.**

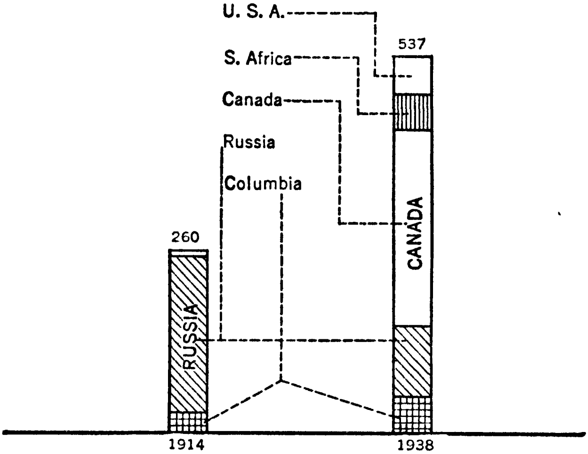


Fig. 152. World production of platinum metals. Thousands of ounces.

Platinum is usually prepared by first dissolving the ore or native alloy in aqua regia, and then evaporating the solution to dryness, chloroplatinic acid ($H_2PtCl_6$) being obtained. The residue is dissolved in water, acidified with hydrochloric acid, filtered, and the platinum precipitated as **ammonium chloroplatinate** by the addition of ammonium chloride:

$$H_2PtCl_6 + 2NH_4Cl \rightarrow (NH_4)_2PtCl_6 \downarrow + 2HCl.$$

By igniting $(NH_4)_2PtCl_6$, spongy platinum is obtained, which may be fused in the electric furnace or by the oxyhydrogen flame, a lime crucible being employed.

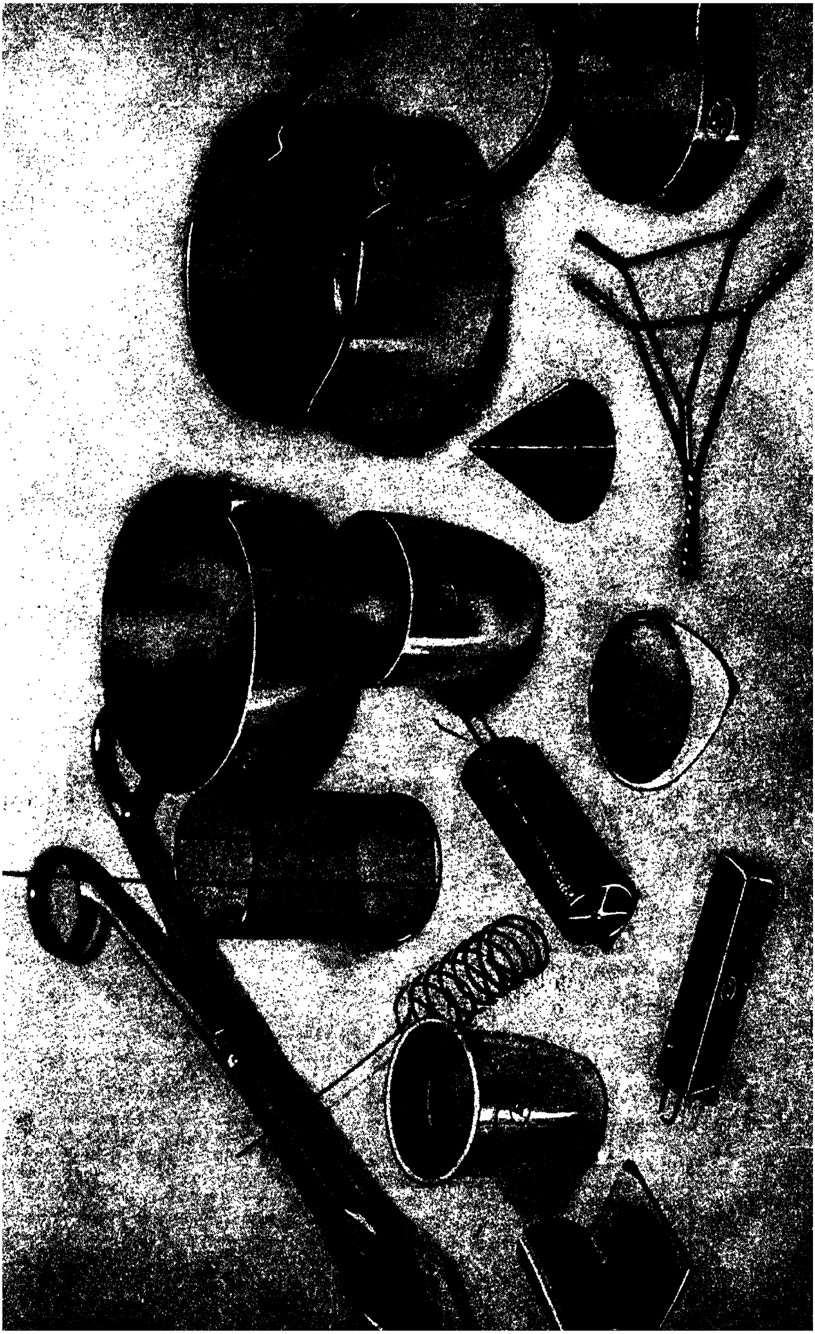
Iridium, present as an impurity, is precipitated in the same form as the platinum. As a rule, therefore, the platinum of commerce is not pure; it usually contains about 2 per cent of iridium. This alloy was formerly used in Russian coinage, and is very valuable for chemical ware, as it is more resistant to acids than is pure platinum.

**451. Properties of Platinum.**—Pure platinum (page 497) has a tin-white color, a density of 21.45, and melts at 1,755°. It is one of the most malleable and ductile of the metals, and can be welded at a white-heat. The metal forms solid solutions with such metals as gold, iron, and copper, which are usually harder than the constituent metals. Thus, gold is hardened by adding about 10 per cent of platinum; this alloy is used for making gold springs in dentistry. Platinum is a good conductor of electricity.

Finely divided platinum, or spongy platinum wire of small diameter, adsorbs or condenses certain gases (49). Thus, a mixture of hydrogen and oxygen will explode in the presence of platinum (catalyst). Platinum also condenses the vapor of methyl alcohol. Certain gas-lighters and cigar-lighters are constructed on this principle (explain more fully).

Hydrogen gas passes through hot sheet platinum. It is not safe, therefore, to heat in a gas flame any readily reducible oxide in a platinum crucible.

*Courtesy of the American Platinum Works*



Platinum has almost the same coefficient of expansion as glass and wires of platinum may therefore be sealed into glass tubes.

Platinum retains its luster when heated to high temperatures in air or oxygen or in contact with water. It is scarcely attacked by hot nitric acid, but is appreciably attacked by hot concentrated sulfuric acid. The metal dissolves readily in aqua regia and interacts with chlorine to form the tetrachloride ($PtCl_4$). It is attacked by fusion with the caustic alkalies or nitrates, by alkali cyanides, phosphorus, arsenic, antimony, etc. Great care should be exercised, therefore, in the use of platinum ware.

**452. Platinum Compounds.**—When platinum is dissolved in aqua regia and the excess of nitric acid removed by evaporation, brownish-red crystals of **chloroplatinic acid**, $H_2PtCl_6, 6H_2O$, are obtained. When heated to 300°, this acid decomposes:

$$H_2PtCl_6 \rightarrow 2HCl + \underset{\substack{\text{Platinous} \\ \text{chloride}}}{PtCl_2} + Cl_2.$$

When asbestos is soaked in a solution of $H_2PtCl_6$, and then ignited, finely divided platinum is deposited on the fiber. The product is known as **platinized asbestos**; it is an excellent catalyst.

When a solution of chloroplatinic acid is treated with a solution of a potassium salt, such as potassium chloride, a reddish-yellow crystalline precipitate of **potassium chloroplatinate** is obtained:

$$H_2PtCl_6 + 2KCl \rightarrow K_2PtCl_6 \downarrow + 2HCl.$$

The salt is sparingly soluble in water, but practically insoluble in 75 per cent alcohol. Ammonium salts behave in a similar way, forming $(NH_4)_2PtCl_6$. The corresponding sodium salt is soluble, however, in dilute alcohol, and much more soluble in water.

Chloroplatinic acid is used as a reagent in separating potassium or ammonium from sodium. When $(NH_4)_2PtCl_6$ is heated, metallic (spongy) platinum is obtained (equation).

## PALLADIUM ${}^{106.7}_{46}Pd$

**453. Palladium, Pd.**—*Palladium* (after *Pallas*, a planetoid discovered in 1802) was announced by Wollaston in 1804. The metal is contained in most platinum ores, and is often found alloyed with gold. It is obtained from platinum ores, as well as from the electrolytic muds which are obtained as by-products in the refining of certain ores of nickel.

Palladium resembles platinum and silver.

Palladium adsorbs very large volumes of hydrogen, the amount under exceptional conditions being as high as 900 volumes. The adsorbed hydrogen is exceedingly active. Thus, a charged palladium electrode, when immersed in a solution of cupric sulfate, precipitates the copper readily (explain).

Palladium is more basic than the other elements of the platinum family. It dissolves in nitric acid, forming the nitrate $Pd(NO_3)_2$.

Palladium is employed for the preparation of graduated surfaces for scientific instruments, for it has a silver-white color and does not tarnish. Gold-palladium alloy is used extensively in dentistry as a substitute for gold-platinum alloy. The metal also is employed as a catalyst: *e.g.*, for the hydrogenation of certain unsaturated carbon compounds; also, as a reducing agent (palladium-hydrogen electrode).

### IRIDIUM $^{193.1}_{77}\mathrm{Ir}$

**454. Iridium.**—*Iridium* (Greek or Latin, *iris*, a rainbow, from the varying tint of its salts) was discovered, along with osmium, by Tennant in 1803. It occurs in platinum ores, as the alloys are usually relatively rich in iridium. Being insoluble in aqua regia, they are left behind when platinum ores are treated with the solvent.

Iridium is a silver-white, hard and brittle metal. It has a density of 22.4 (nearly as heavy as osmium).

An alloy of iridium and osmium is used in producing tips for gold pens (*iridosmine*). It also is used for hardening platinum and for rendering it more resistant to corrosion. Platinum-iridium alloys are used extensively in electrical work. The *standard meter bar*, kept at the International Bureau of Weights and Measures at Sèvres, is an alloy of platinum and iridium.

### THE LESS IMPORTANT MEMBERS: Ru, Rh, Os

**455. Ruthenium, Ru.**—*Ruthenium* (*Ruthenia*, Russia) was proved by Claus (1845) to be present in platinum ores from the Ural. The metal also is found in *iridosmine* (an alloy containing iridium and osmium). The production of the metal is small.

Ruthenium is a dark gray (or nearly black) hard, brittle, heavy metal. At high temperatures it is attacked by oxygen, thus showing a relationship to iron. The pure metal is very resistant to the action of acids, but combines with chlorine at a high temperature.

**Ruthenium tetroxide,** $RuO_4$, is formed when the metal is heated in oxygen at 1,000°. This compound is yellow in color, melts at about 26°, and is volatile with steam.

**456. Rhodium, Rh.**—*Rhodium* (Greek *rhodon*, a rose, from the rose-red color of its salts) was discovered by Wollaston in 1804. The metal has the appearance of aluminum, but is much heavier. It is very resistant to corrosion by acids, but is more readily attacked by free chlorine than are the other metals of the triad.

Chemical apparatus has been constructed of pure rhodium, as well as of an alloy of the metal (*rhotanium*). It also is used in tipping gold pens and in electric pyrometers.

An alloy of rhodium and platinum constitutes the positive element of certain thermo-couples.

**457. Osmium, Os.**—*Osmium* (Greek, meaning *a smell*, because of the peculiar odor of its volatile oxide, $OsO_4$) was discovered by Tennant in 1803. He found it to be present in a metallic residue which is obtained when platinum ores are dissolved in aqua regia. Osmium is found in iridosmine or osmiridium (an alloy of osmium and iridium) and in native platinum. It is interesting in being the heaviest of known bodies (density, 22.48).

When finely divided, it oxidizes somewhat readily. Crystalline osmium resists the action even of aqua regia, but the amorphous metal dissolves in fuming nitric acid, and more slowly in aqua regia.

Osmium is chiefly acid-forming in character.

**Osmium tetroxide,** $OsO_4$, is commonly called "osmic acid," although it does not play the role of an acid anhydride. It may be obtained by heating finely divided osmium in air to a temperature of about 400°, the osmium burning to form a highly poisonous vapor! Like the corresponding ruthenium compound, it is volatile with steam, the vapor having a very irritating and disagreeable smell, somewhat similar to that of chlorine. It is used in biology for staining and hardening tissues, the oxide being reduced to metallic osmium.

458. TABLE 98. USES FOR GROUP VIII COMPOUNDS

| | |
|---|---|
| **Iron and its compounds** | **Fe (437); $Fe(OH)_2$, $Fe(OH)_3$; $FeSO_4, 7H_2O$; $Fe_2O_3$ (438); inks, blue printing, Turnbull's blue, Prussian blue, ferri- and ferrocyanides (439).** |
| Ferric acetate, basic $Fe(OH)(CH_3COO)_2$ | in medicine, mordant. |
| Ferrous ammonium sulfate, Mohr's salt $(NH_4)_2SO_4, FeSO_4, 6H_2O$ | reducing agent for standardizing potassium permanganate solutions as described in (416). |
| Ferric chloride $FeCl_3, 6H_2O$ | deliquescent yellow salt, mordant, oxidizing agent, medicinal; alcoholic solution is tincture of iron. |
| Ferric nitrate $Fe(NO_3)_3, 9H_2O$ | mordant. |
| Iron phosphates | ferric phosphate $FePO_4, 4H_2O$ and ferrous phosphate $Fe_3(PO_4)_2, 8H_2O$; in medicine. Also other phosphorus salts. |
| **Cobalt and its compounds** | **Co (440); stellite (441); complex cobalt salts (442).** |
| Cobaltic oxide $Co_2O_3$ | grey powder, insoluble in water, dissolved by acids; ceramic pigment (*i.e.*, cobalt blue). |
| Cobaltous acetate $Co(CH_3COO)_2, 4H_2O$ | deliquescent pink salt; pigment, preparing cobalt compounds. |
| Cobaltous carbonate $2CoCO_3, 3Co(OH)_3$ | for preparing cobalt salts and pigments. |
| Cobaltous chloride $CoCl_2, 6H_2O$ | cherry-red soluble salt; electroplating. |
| Cobaltous driers | cobalt linoleate, resinate, oleate, etc., as paint driers. |
| Hopcalite | mixture of oxides of Co, Mn, Cu and sometimes Ag; gas-mask catalyst to oxidize CO. |
| **Nickel and its compounds** | **Ni, carbonyls (443–5); Monel, Invar, Nichrome, Permalloy (444); with dimethyl-glyoxime (446).** |
| Nickelous carbonate $NiCO_3, 2Ni(OH)_2, 4H_2O$ | soluble in ammonium salts and acids; insoluble in water; green glazes, making Ni-salts. |
| Nickelous chloride $NiCl_2, 6H_2O$ | green, deliquescent salt, very soluble, antiseptic, absorbent for $NH_3$ in gas masks. |
| Nickelous oxide NiO | green, insoluble; forming catalyst, ceramics; forms $Ni_2O_3$ on heating in oxygen. |
| Nickelous sulfate $NiSO_4, 6H_2O$ | green; nickel plating, mordant, ceramics, making organic nickel driers. See 444. |
| **Platinum and its compounds** | **Pt, $PtAs_2$ (449); chloroplatinates (450–2) $PtCl_4$ (451).** |
| Barium platinocyanide $BaPt(CN)_4, 4H_2O$ | fluorescent X-ray screen. |
| Platinic chloride $PtCl_4, 5H_2O$ | red crystals; from $Cl_2$ on Pt, plus water; decomposes above 500°. |
| Potassium chloroplatinite $K_2PtCl_4$ | rose-red crystals by reducing $K_2PtCl_6$, potassium chloroplatinate; for Pt silver finishing in photography. |
| **Other members of the Pt family** | **Pd, $Pd(NO_3)_2$ (453); Ir, iridosimine (454); Ru, $RuO_2$ (455); Rh, rhotanium (456); Os, $OsO_4$ (457).** |
| **Palau** | **a Pd-Au alloy.** |

## QUESTION REVIEW

### I. THE IRON FAMILY: Fe, Co, Ni. (436).

1. Describe these properties for Fe, Co and Ni: approximate boiling points and densities; rusting characteristics, relative stabilities of their salts, two other general chemical properties.

**a. Iron** (437–8). **Inks and blueprints** (439).

2. Contrast the properties of iron and steel. Why cannot passive iron be utilized industrially?
3. Write formulas for: potassium ferrocyanide, ferrous ferricyanide, Turnbull's blue, Prussian blue, laundry bluing.
4. If an ink stain were soaked in ammonium oxalate and the solution exposed to sunlight, what would be formed?

**b. Cobalt** (440–2).

5. Show by equations the smelting of smaltite.
6. What properties has Stellite? anhydrous cobaltous chloride?
7. Write the formulas for: potassium dichloro-tribromo-ammino-cobaltate. For bromo-nitro-triaquo-ammino-cobalti-iodide. What precipitate would be obtained upon adding silver nitrate to each? Explain.

**c. Nickel** (443–5).

8. Give equations showing the metallurgy of pentlandite. Who has a monopoly on nickel?
9. What properties of each of the following qualify it for its particular use: Monel metal, Invar, Nichrome, Permalloy?
10. What volatile compounds do the members of the iron family form? To what industrial use is this property of volatility put?

**d. Analysis of the iron family** (446).

11. Identify the use of the following in analysis: KCNS, potassium ferro- and ferri-cyanides, potassium nitrite, dimethylglyoxime; $(NH_4)_2S$; $NH_4OH$.

### II. THE PLATINUM FAMILY

**a. General** (447). **Occurrence** (448). **Uses** (449).

12. Draw up a table contrasting the boiling points and densities of the three most important members of this group.
13. Why has Canada become a chief producer? In Alaskan creek sediments what three members are most abundant? Compare this with their consumption and price.

14. Outline three uses for Pt, and one each for the other members of the family.

**b. Platinum (450-452). Palladium (453). Iridium (454).**

15. Describe the preparation of ammonium chloroplatinate from native ore. Write an equation showing what occurs when this is heated.
16. Relate the properties of platinum as regards: permeability to gases, resistance to acids and alkalies, malleability.
17. What complex platinum salt may be used in chemical analysis, *i.e.*, by forming insoluble salts?

**c. The less important members: Ruthenium (455), Rhodium (456), and Osmium (457).**

III. USES FOR GROUP VIII COMPOUNDS (458).

18. Name and give a use for compounds in this group.

**Reading References:** Articles in the Appendix:

*Iron group:* 11, 30, 49, 78 and 122.
*Platinum group:* 19, 49, 78, 204, 219 and 228.

# CHAPTER XXXIII

# BORON AND SILICON

**459. The Non-Metals.**—Having just concluded a study of the *metals* in the Periodic Table, we shall turn to the *non-metals.*

TABLE 99. THE NON-METALS

| I | II | III | IV | V | VI | VII |
|---|---|---|---|---|---|---|
| | | B | C | N | O | F |
| | | | Si | P | S | Cl |
| | | | | As | Se | Br |
| | | | | Sb | Te | I |
| | | | | Bi | Po | — |

In certain respects these elements differ strikingly from the metallic elements. Some are gases at room temperature: nitrogen (N), oxygen (O), fluorine (F) and chlorine (Cl). Bromine (Br) is a liquid. The remainder are solids. The higher in any column, and the farther to the right in the table as a whole, the less metallic is the element. From this it follows that fluorine is the most active of all non-metals. On the other hand tellurium (Te) and iodine (I) look not unlike metals; while arsenic (As), antimony (Sb) and bismuth (Bi) have a metallic luster and tend to be amphoteric, but they too are non-metals. Many of them exist in several forms (*e.g.*, diamond, graphite, and amorphous carbon); this includes boron, silicon, carbon, phosphorus and the sulfur family.

Most of the non-metals form hydrides; oxides are numerous; and these oxides dissolve in water to form acids, the non-metal remaining in the anion:

| | | | | | |
|---|---|---|---|---|---|
| hydrides | $B_2H_6$ | $CH_4$ | $NH_3$ | $H_2O$ | $HCl$ |
| oxides | $B_2O_3$ | $CO_2$ | $N_2O_5$ | $SO_3$ | $Cl_2O_7$ |
| acids | $H_3BO_3$ | $H_2CO_3$ | $HNO_3$ | $H_2SO_4$ | $HClO_3$ |

In the oxy-acids of any particular non-metal, such as $HClO$, $HClO_2$, $HClO_3$, and $HClO_4$, increase in number of oxygen atoms increases the strength of the acid; *i.e.*, $HNO_3$ is stronger than $HNO_2$, and $H_2SO_4$ is stronger than $H_2SO_3$.

**460. Boron and Silicon.**—It will be recalled that beryllium (336) was quite unlike the other members of the II-A group. For example, the beryllium ion does not react with hydrogen or with steam as the other alkaline earths do; its molten halides are poor conductors, and they hydrolyze; its fluoride is insoluble. These anomalies are attributed to the abnormally small size of the beryllium ion, which tends to bind it tightly to other ions.

In the same way the smallness of the boron ion causes it to behave unlike the metal aluminum which follows it in group III-B; and carbon and silicon behave unlike tin and lead which are below them in group IV-B. Instead, **boron and silicon are non-metals** with very similar properties. Carbon, which is above silicon in the III-A group, will be taken up later; it has unusual properties and forms a separate world of chemistry (organic chemistry).

Unlike aluminum hydroxide, which is amphoteric, the compound $B(OH)_3$ acts only as an acid, *i.e.*, boric acid, $H_3BO_3$. In most of its chemical relations boron resembles carbon and silicon more closely than it resembles aluminum. All of them exhibit allotropic forms, and combine directly with oxygen at a high temperature to form anhydrides of feeble acids—$B_2O_3$, $CO_2$, and $SiO_2$. Carbon and silicon are much more abundant than boron and are more widely distributed in nature.

## BORON $^{10.82}_{5}B$

**461. History and Occurrence.**—Boron was first prepared independently by Gay-Lussac and Thénard and by Davy, about 1808, by the reduction of boron trioxide with potassium. Boric acid was first prepared from borax by Homberg in 1702.

Following the discovery of borate deposits in California in 1920 that state became the world's chief producer. The minerals there consist of **borax**, $Na_2B_4O_7$, $10H_2O$; and **colemanite**, $Ca_2B_6O_{11}$, $5H_2O$. In 1926 a rich deposit was discovered, by C. M. Razor, of a mineral **razorite** or **kernite**, $Na_2B_4O_7$, $4H_2O$, in the Mohave Desert, California, 400 feet below the surface, and 80 feet thick. As a result of this activity in California, the price of borax has tumbled from $150 a ton in 1920 to $30 in 1940.

Before these deposits were uncovered, Germany supplied the mineral **boracite**, $2Mg_3B_8O_{15}$, $MgCl_2$; but in 1938 that country herself imported 50,000 tons of crude borax from the United States. Probably the most interesting source is from the jets of steam and hot gases in the Italian volcanic region in Tuscany, where the "*soffioni*" issuing from the cracks contain ammonia, carbon dioxide, and 0.1 per cent or less of **boric acid,** $H_3BO_3$. Many years ago impure borax, known as *tincal,* was exported from Tibet.

249,976 tons of borax, colemanite, kernite, and boric acid were produced in the United States in 1939; 37 per cent of this was exported.

**462. Preparation.**—Boron may be prepared by heating boron trioxide with magnesium (Moissan):

$$B_2O_3 + 3Mg \rightarrow 2B + 3MgO.$$

The magnesium oxide may be dissolved in hydrochloric acid, leaving boron as an amorphous brown powder. Sodium or potassium may be substituted for magnesium. Boron thus prepared is not pure. By heating $B_2O_3$ with excess of powdered aluminum, crystals of boron containing aluminum are found in the solidified mass. The metal may be dissolved in dilute hydrochloric acid.

Boron in the purest state is prepared by reducing boron trichloride with hydrogen in the high-tension electric arc (Weintraub):

$$2BCl_3 + 3H_2 \rightarrow 2B + 6HCl.$$

**463. Properties.**—**Amorphous boron** is a dark-brown powder of sp. gr. 1.73; its melting point is 2,300°, and it is a poor conductor at ordinary temperatures. At 400° its conductivity for electricity is over 2,000,000 times that at ordinary room temperature. In contrast, metals are better conductors at low than at high temperatures.

Boron is an active element at high temperatures; it burns in air at 700° to form $B_2O_3$ and BN. Boron unites directly with fluorine, chlorine, and bromine. At the temperature of the electric arc it combines with carbon to form a carbide, $B_6C$, which stands next to the diamond in hardness.

The **crystalline form of boron** has a sp. gr. of 2.3, and is hard enough to scratch both ruby and corundum; it is more resistant to the action of reagents than is amorphous boron. The luster and hardness of crystalline boron are near that of the diamond.

**464. Boric Acid, $H_3BO_3$.—a. Preparation.** For a hundred years boric acid has been obtained from the volcanic gases in Tuscany. The steam jets are surrounded by basins, into which a water solution of $H_3BO_3$ condenses; this is further concentrated in lead pans which are heated by the hot volcanic gases. Upon cooling the liquid, impure crystals of $H_3BO_3$ are obtained; and these may be further purified by recrystallization. The Tuscan lagoons have supplied the European market with much of its boric acid.

The acid is also prepared by treating borax with HCl:

$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4H_3BO_3 \downarrow .$$

Boric acid is a white crystalline substance, which separates from aqueous solution in thin, lustrous flakes, belonging to the triclinic system; they are greasy to the touch. It is seven times more soluble in water at 100° (28.7 parts per 100 g.) than at 20°.

**b. Chemical properties.** Boric acid is a feeble acid, ionizing to form $H^+$ and $H_2BO_2^-$. Heated, it loses water and finally forms the oxide $B_2O_3$:

$$\underset{\text{Orthoboric acid}}{H_3BO_3} \overset{100°}{\rightleftarrows} \underset{\text{Metaboric acid}}{HBO_2} \overset{140°}{\rightleftarrows} \underset{\text{Tetraboric acid}}{H_2B_4O_7} \overset{\text{High temp.}}{\rightleftarrows} \underset{\text{Boric anhydride}}{B_2O_3}$$

**Boron oxide** is not volatile below white heat; so that when it is heated with salts, the salts decompose and a borate is formed, *e.g.*,

$$2B_2O_3 + K_2SO_4 \xrightarrow[\text{temp}]{\text{high}} K_2B_4O_7 + SO_3.$$

DEMONSTRATION 123. BORIC ACID TEST

Materials: 100 cc. of ethyl alcohol containing a pinch of boric acid in a 250 cc. Erlenmeyer flask over burner; stopper with 6-mm. tube drawn to a nozzle; turmeric paper, solution of boric acid, sodium hydroxide.

**c. Analysis.** When boric acid is heated with alcohol, the vapor burns with a fine green flame—a delicate test for the acid. A solution of boric acid, or a borate acidified with hydrochloric acid, turns turmeric paper reddish brown, particularly when the paper is dried. When an alkali is brought in contact with the paper, it turns dark. This is a sensitive test for boric acid.

**d. Uses.** Boric acid is a very mild antiseptic. A 2 per cent solution is used as an eye-wash, and is sold as *boracic acid.* Its use as a food preservative is now forbidden in the United States. Its greatest uses are those listed below for borax.

**465. Borax.**—Borax is applied loosely to all of the hydrates of sodium tetraborate, although the deca-hydrate, $Na_2B_4O_7, 10H_2O$, is the one traded in commerce.

**a. Occurrence and preparation.** Sodium tetraborate occurs in the United States in the Mohave Desert as $Na_2B_4O_7, 4H_2O$; when crystallized from water the decahydrate ($10H_2O$) is obtained *below* 56°, and the pentahydrate ($5H_2O$) *above* that temperature.

The crude tetrahydrate from the Mohave Desert contains about 25 per cent clay, which is readily removed by recrystallization; this yields the decahydrate, $Na_2B_4O_7, 10H_2O$.

Borax is also manufactured from the other natural borates (colemanite in California, boracite in Stassfurt, boric acid in Tuscany) by fusing with sodium carbonate, leaching with water, and crystallizing out the decahydrate:

$$\underset{\text{colemanite}}{Ca_2B_6O_{11}, 5H_2O} + 2Na_2CO_3 \xrightarrow{\text{fused}} Na_4B_6O_{11} + 2CaCO_3 + 5H_2O;$$

$$2Na_4B_6O_{11} + 31H_2O \rightarrow \underset{\text{borax}}{3Na_2B_4O_7, 10H_2O} + 2NaOH.$$

**b. Properties and uses.** The decahydrate consists of large monoclinic crystals which dissolve in water to turn litmus blue. The pentahydrate is octahedral.

### DEMONSTRATION 124. BORAX BEADS

Materials: Pt-wire loop on glass rod, burner, solid salts of borax, solid salts of Co, Cu, Fe, Mn, and Ni.

When borax is heated in a loop of platinum wire to a high temperature it fuses into a transparent bead without decomposing. If this bead is dipped into salts of metals and reheated, the salts are decomposed to form mixed meta-borates, *e.g.*,

$2NaBO_2, Co(BO_2)$ · · · cobalt blue · · · borax bead

and from the colors of the **borax beads** the metals in the salts can be identified. This is a handy method of analysis for prospectors.

During the past two decades the use of borax has increased three-fold due to its use in heat-resisting Pyrex glass (478c). Borax is also used in hard soldering, welding iron, in the manufacture of glazes, enamels and soaps, in the laundry, in degumming silk, for preserving meat, etc.

In research, borate buffer solutions which hold the solution to a constant pH are well known.

## SILICON $^{28.06}_{14}Si$

**466. Occurrence.**—Next to oxygen, silicon is the most abundant element, constituting a little more than one-fourth of the mass of the earth's crust. The element does not occur in the free state, but in combination with oxygen and other elements it is very widely distributed. Since silicon compounds play such an important part in the formation of the minerals and rocks which constitute so much of the earth's crust, it may be regarded as the central element of the Inorganic Kingdom, just as carbon is the central element of the Organic Kingdom.

**Silica and silicates are the most abundant minerals constituting the earth's crust.**

**Rocks** are the fundamental units of geology, and are either simple minerals or aggregations of minerals. Rocks are usually mixtures and are therefore variable in composition. Thus, *granite* is a mixture of quartz, feldspar and mica; all of these contain silicon, which is therefore an element of utmost importance to the mineralogist and geologist.

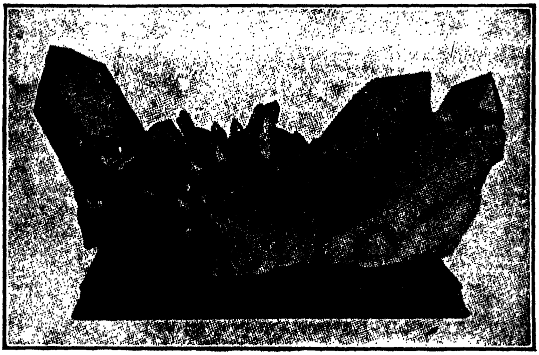


FIG. 153. Quartz crystals from Magnet Cove, Arkansas. Jesup gift, American Museum of Natural History.

**467. Preparation.**—Silicon was first prepared by the Swedish chemist Berzelius, in 1823.

It may be prepared in the laboratory by strongly heating finely ground silicon dioxide (quartz, sand) with either magnesium or aluminum (thermit reaction):

$$3SiO_2 + 4Al \rightarrow 3Si + 2Al_2O_3,$$
$$SiO_2 + 2Mg \rightarrow Si + 2MgO.$$

The first reduction is carried out in an excess of aluminum, and Si crystallizes out in the molten metal. With the reduction with magnesium, a small quantity of magnesium silicide, $Mg_2Si$ is also formed; the silicon is obtained as a brown powder. In either instance the Si may be freed by treating with hydrochloric acid, which dissolves the Al or MgO.

Silicon is prepared industrially by heating silica and coke to a high temperature in the electric furnace; if an excess of carbon is used, silicon carbide SiC is formed (505).

$$SiO_2 + 2C \rightarrow Si + 2CO.$$

However, silicon is rarely prepared in this free state. Instead, for the steel industry an iron-silicon alloy, **ferrosilicon**, is manufactured by heating a mixture of $Fe_2O_3$, carbon, and $SiO_2$ in the electric furnace. Both oxides suffer reduction. For 1939 the domestic consumption of ferrosilicon (343,922 tons) in making special steels exceeded that of ferromanganese, ferrovanadium, or any other similar alloy (Table 94, section 435).

**468. Properties and Uses.**—The so-called "amorphous" silicon, the brown powder mentioned in the foregoing section, is shown by X-ray analysis really to be crystalline and different from large crystals of silicon only in the fineness of its subdivision.

Silicon is a gray-black, lustrous, brittle substance, density only 2.4; it is exceedingly hard, easily scratching glass.

The non-metal is very reactive at high temperatures, combining directly with most of the elements to form **silicides,** *e.g.*, $Mg_2Si$ magnesium silicide, and **silicon compounds,** *e.g.*, $SiO_2$, silicon dioxide; $SiF_4$ and $SiCl_4$, silicon halides; SiC silicon carbide, or carbon silicide. Silicon is dissolved by hot caustic alkalies, ferrosilicon (as *hydrogenite*) being a light-weight source of military hydrogen:

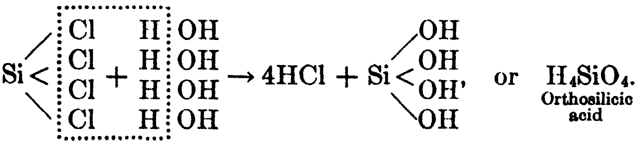
$$(Fe)Si + 4NaOH \rightarrow Na_4SiO_4 + 2H_2 \uparrow + (Fe).$$

Aside from its important use in ferrosilicon steel, the element is used as a deoxidizer (**428**); in new aluminum alloys; and in duriron, a silicon alloy for chemical containers which resists acid corrosion.

**469. Silicon Halides.**—Silicon tetrachloride is prepared by passing chlorine gas through a heated mixture of silica and carbon:

$$SiO_2 + 2C + 2Cl_2 \rightarrow SiCl_4 + 2CO.$$

It is a colorless liquid, boiling at 58°. When brought into contact with moist air, it *hydrolyzes*, forming hydrochloric acid and orthosilicic acid:



$$Si\begin{cases}Cl\\Cl\\Cl\\Cl\end{cases} + \begin{matrix}H \vdots OH\\H \vdots OH\\H \vdots OH\\H \vdots OH\end{matrix} \rightarrow 4HCl + Si\begin{cases}OH\\OH\\OH\\OH\end{cases}, \quad \text{or} \quad \underset{\text{Orthosilicic acid}}{H_4SiO_4}.$$

Smoke clouds for war or "skywriting" are often made of silicon tetrachloride and ammonia; in addition to the clouds of orthosilicic acid, white clouds of $NH_4Cl$ are formed. (Write equations.)

**Silicon tetrafluoride** is formed during the etching of glass, such as in the frosting of lamp bulbs:

$$\underset{\substack{\text{quartz}\\\text{glass}}}{SiO_2} + 4HF \rightarrow \underset{\text{a gas}}{SiF_4} \uparrow + 2H_2O.$$

The tetrafluoride, is a colorless gas, readily decomposed by water, forming silicic acid and fluosilicic acid ($H_2SiF_6$):

$$3SiF_4 + 4H_2O \rightarrow H_4SiO_4 + 2H_2SiF_6.$$

Silicic acid may be removed by filtration, a solution of fluosilicic acid being left. This acid is known only in solution, for when its solution is concentrated by evaporation, silicon tetrafluoride is given off:

$$H_2SiF_6 \rightarrow SiF_4 \uparrow + H_2F_2.$$

Most of the salts of fluosilicic acid are soluble in water, conspicuous exceptions being $K_2SiF_6$ and $BaSiF_6$, which are sparingly soluble in water and insoluble in alcohol. The acid is therefore used in analysis for separating certain of the metals.

### SILICON DIOXIDE

**470. Occurrence.**—Silicon dioxide is widely distributed and abundant. The chief forms of silica, which are more or less pure, are as follows:

(I) *Crystalline*

Rock Crystal
Amethyst
Smoky Quartz
Tridymite

(II) *Massive*

Quartzite
Rose Quartz
Agate
Jaspar
Carnelian
Flint
Chalcedony
Opal

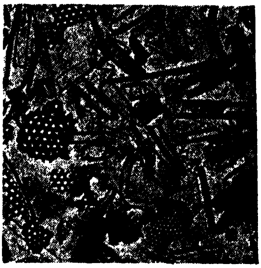
(III) *Fragmentary*

Sea Sand
Gravel
Pebbles
Sandstone
Conglomerate

The colored varieties of silica owe their color to small quantities of impurities. Thus, the color of *amethyst* is due to manganese and iron, and that of smoky quartz to organic matter. *Opal* and *flint* are slightly hydrated forms of silica.

**Infusorial earth** or **diatomaceous earth** is an opal-like secretion of organisms mined chiefly in California and Oregon; also, Denmark, Algeria and Germany (*kieselguhr*). About 100,000 tons are produced each year in the United States as (*a*) an abrasive and polish, (*b*) a heat-insulator, (*c*) a filtration medium, and (*d*) a filler for plastics, paints and compositions. The Johns-Manville product is known as **celite.** The finely sculptured skeletons of these motile plants (Fig. 154) are used as a critical test for optical instruments. **Tripoli,** including Philadelphia rottenstone, is another silica abrasive, and is used as a substitute for diatomite.

**Quartz** is mined in a great number of states, especially Arizona, California, North Carolina and Virginia. Its use for sandpaper and in metallurgical plants called for 34,959 tons in 1939, double the 1935 consumption.



*Courtesy of Johns-Manville*

FIG. 154. Photomicrograph of infusorial earth.

**471. Properties.**—**Quartz** crystallizes in six-sided prisms capped with pyramids; its sp. gr. is 2.65 and the hardness is 7. Clear crystals of quartz are used in the manufacture of optical instruments and spectacles. The melting point of quartz is 1,670°; therefore it fuses in the oxyacetylene flame and in the electric furnace. Chemical apparatus is now manufactured by fusing quartz. When it is fused in the oxyhydrogen or oxyacetylene flame, the product is transparent; but when fused in the electric furnace, gas bubbles appear, giving articles made from it a milky appearance.

DEMONSTRATION 125. PROPERTIES OF QUARTZ

Materials: Tubing of quartz, Pyrex brand glass, Vycor brand glass, soft glass; burner, 2 liter beaker of cold water, silica ware, tongs.

Quartz has the lowest coefficient of expansion of any known substance (0.000000449 between 0° and 1,000°); therefore quartz vessels may be heated to redness and suddenly chilled without cracking. This may be strikingly shown by heating a quartz dish or tube to redness and then plunging it into ice water. "Silica ware" is employed in considerable quantities.

The action of hydrofluoric acid upon quartz has already been described (469). Molten **alkali** hydrosulfides or **alkali carbonates** attack quartz, clay, feldspar and other siliceous rocks and convert them into soluble silicates; this is an important device for preparing analytical solutions of otherwise insoluble rocks.

$$SiO_2 + 4KOH \rightarrow K_4SiO_4 + 2H_2O,$$
$$SiO_2 + Na_2CO_3 \rightarrow Na_2SiO_3 + CO_2.$$

**472. Fused Quartz.**—Clear fused quartz is now produced industrially by means of an electric vacuum furnace. Very pure quartz is melted in the furnace, the quartz flowing away in the form of rods or tubing. Indeed, comparatively large masses of perfectly clear quartz may be produced. It is remarkable for its transparency to rays of the visible spectrum, to long or infrared rays, and to the short ultra-violet rays. For this purpose it is made into prisms and windows for photochemical research. Quartz, like some of the recent plastics (629), possesses the property of bending light around corners by internal reflection; a thirty-foot rod will convey the light of a match from one end to the other.

**473. Silicic Acids.**—Since $SiO_2$ is the oxide of a non-metal we should expect it to form oxy-acids. (Compare $CO_2$ giving $H_2CO_3$.) Silicic acids are well known, but any attempt to separate them from water fails: they always decompose irreversibly into silicon dioxide according to the scheme:

$$\underset{\text{ortho-silicic acid}}{H_4SiO_4} \xrightarrow{-H_2O} \underset{\text{meta-silicic acid}}{H_2SiO_3} \xrightarrow{-H_2O} SiO_2.$$

Other silicic acids are known; they all lose water to form silicon dioxide. Two examples are:

disilicic acid $H_6Si_2O_7 \rightarrow 3H_2O + 2SiO_2$,
trisilicic acid $H_4Si_3O_8 \rightarrow 2H_2O + 3SiO_2$.

These are called **condensed acids**: condensation is a term applied when several units combine with the elimination of water, and the disilicic acid may be considered a condensation of two meta-silicic acid molecules; whereas trisilicic acid comes from the condensation of three ortho-silicic acid units. (Write the equations). Al, K, Na, and Ca minerals of these acids abound in nature (474). The silicic acids are all feeble acids.

### DEMONSTRATION 126. SILICIC ACID GEL

Materials: Concentrated HCl, water-glass diluted with an equal volume of water in a 2-liter beaker; 400 cc. beaker; 150 cc. beaker.

When an alkali silicate is treated with concentrated HCl, a gelatinous mass of $H_2SiO_3$ is obtained:

$$Na_2SiO_3 + 2HCl \rightarrow 2NaCl + H_2SiO_3.$$

If the order of mixing is reversed, *i.e.*, if the solution of silicate is poured into concentrated HCl, no precipitate appears; the silicic acid remains suspended in a colloidal condition (671). If much of the water is expelled from the gel, a material with enormous surface is obtained: **silica gel.** It is used for absorbing gases, as a catalyst, and as a catalyst supporter.

In quantitative analysis of a silicate rock the rock is fused in a platinum crucible with $Na_2CO_3$, forming soluble $Na_2SiO_3$; subsequent treatment with HCl gives soluble metal chlorides and silicic acid; when this is heated to dryness the latter decomposes into insoluble $SiO_2$. The metal chloride goes into solution upon treating with water, leaving $SiO_2$ as a residue.

### SILICATES

**474. Silicate Rocks.**—Some of the most important naturally occurring silicates in the mineral kingdom are given below. Many rocks are mixtures of these; *e.g.*, **trap rock** contains feldspars and silicates of calcium and magnesium, and **granite** is a mixture of quartz, feldspar and mica.

| | |
|---|---|
| (I) *Metasilicates*<br>(Salts of $H_2SiO_3$) | $CaMg_3(SiO_3)_4$ Asbestos<br>$CaSiO_3$, Wollastonite<br>$Mg_3H_2(SiO_3)_4$, Talc or Soapstone |
| (II) *Orthosilicates*<br>(Salts of $H_4SiO_4$) | $Mg_2SiO_4$, Olivine<br>$Al_2H_2(SiO_4)_2 . H_2O$, Kaolin<br>$KAl_3H_2(SiO_4)_3$, Mica |
| (III) *Disilicates: e.g.*, $Mg_3Si_2O_7 . 2H_2O$, Serpentine<br>(Salts of $H_6Si_2O_7$) | |
| (IV) *Trisilicates*<br>(Salts of $H_4Si_3O_8$) | $KAlSi_3O_8$, Potash feldspar (orthoclase)<br>$NaAlSi_3O_8$, Soda feldspar (albite). |

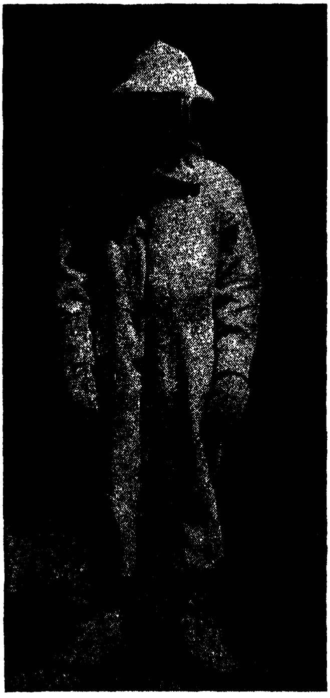
Of special interest and importance in the chemistry of the soil is the weathering of **feldspars** to form clay and potash. Feldspars contain both alumina and silica in combination with a powerful base, such as $K_2O$, $Al_2O_3$, $6SiO_2$ (*i.e.*, $KAlSi_3O_8$):

$$\underset{\text{Feldspar}}{2KAlSi_3O_8} + 2H_2O + CO_2 \rightarrow \underset{\substack{\text{Kaolin}\\ \text{(clay)}}}{H_4Al_2Si_2O_9} + 4SiO_2 + \underset{\substack{\text{Potassium}\\ \text{carbonate}\\ \text{(potash)}}}{K_2CO_3}.$$

**475. Structure of Silicates.**—X-ray studies show that in silicate rocks the silicon is always surrounded by four oxygen atoms, forming tetrahedra of $(SiO_4)^{-4}$ (orthosilicates), or $(SiO_3)^{-2}$ (metasilicates). The metallic ions, $K^+$, $Na^+$, $Al^{+3}$, $Ca^{+2}$, $Mg^{+2}$, etc., are much smaller than the oxygen atoms, and fit into the tetrahedra wherever they can find room. The tetrahedra may be packed together in a variety of ways. (a) In asbestos for instance, giant strings are formed in which the tetrahedra may run from one end of the fibre to the other (Fig. 155).

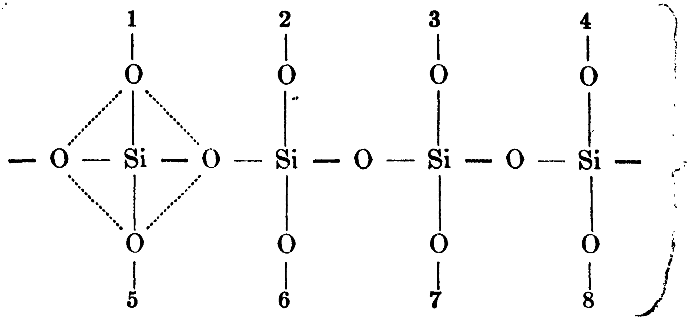
*Courtesy of Johns-Manville*

FIG. 155. Asbestos, a natural rock.



*Courtesy of Johns-Manville*

FIG. 156. An asbestos suit.



Asbestos, $CaMg_3(SiO_3)_4^{-8}$. Only the anion is shown, this giant $SiO_3$-string being feebly joined to parallel giant strings at points 1 to 8 by $Ca^{++}$ and $Mg^{++}$. One tetrahedron is sketched in.

Asbestos forms fibres because the long chains of $SiO_3$ units are held only feebly by the calcium and magnesium ions, while the bonds between the Si and O atoms are considerably stronger.

(*b*) In mica the tetrahedra are arranged in layers like piles of wire netting, which accordingly cleaves easily. (*c*) In the compact feldspars the tetrahedra interlace to form a three-dimensional giant molecule. (*d*) In beryl a ring-shaped lattice is formed. (*e*) The orthosilicates form an ionic lattice composed of metallic ions and tetrahedral ions of $(SiO_4)^{-4}$.

**476. Water Glass.**—This is prepared by (a) fusing powdered quartz or infusorial earth with NaOH or $Na_2CO_3$, or (b) by digesting $SiO_2$ with a boiling solution of NaOH under pressure. The ordinary commercial product varies from $Na_2SiO_3$, $SiO_2$ to $Na_2SiO_3$, $3SiO_2$, the sodium silicate being rendered less alkaline by increasing the proportion of $SiO_2$.

Strictly speaking, water glass is a **soluble glass**; but because of its unique properties it is not being considered under the heading of glasses.

It is used extensively as a filler for soaps; for instance in 1941 Germany required the admixing of 15–45 per cent of sodium silicates in soaps to conserve the edible fats normally used in soap manufacture. Water glass is also used for fire-proofing and waterproofing timbers, as a heat resistant cement, and for preserving eggs. The latter use (1 vol. water glass plus 9 vols. water) depends upon the low solubility of gases in water glass.

## GLASSES

**477. Historical.**—The art of manufacturing glass is very old. The early Egyptians were familiar with it, for glass beads have been found in mummy cases at least 3,000 years old. Glass articles also have been discovered in the excavations of Nineveh. Venice was formerly the center of the industry, but was finally displaced by Bohemia. The Bohemians produced fine crystal glass, and invented the art of engraving on it. Great quantities of glass are manufactured in England, France, Germany, the United States, Belgium, and Austria. Belgium and England have been particularly noted for window and plate glass, and Austria and Germany for blown ware.

Before the Great War, the United States imported from Germany nearly all the glass used in the manufacture of optical instruments. When the foreign supply of optical glass was cut off, our scientists and manufacturers undertook to work out the problem of producing this variety of glass, and before the end of the war our supply was in excess of the needs.

**478. Compositions of Glasses.**—When sand, sodium carbonate and lime are fused in the proper porportions, a clear glass is obtained. Any haphazard mixture of these ingredients will not do; this is amply indicated in Table 100 where the compositions of bottle glass from 1400 B.C. are found to be not particularly different from those of 1941 A.D.

TABLE 100. COMPOSITIONS OF SOME GLASSES

| | QUARTZ | | LIME | | LEAD | ONE TYPE OF PYREX BRAND |
|---|---|---|---|---|---|---|
| | FUSED | VYCOR BRAND | | | | |
| Date first used → | 1920 | 1940 | 1400 B.C. | 1941 A.D. | B.C. | 1918 |
| $SiO_2$ | 100 | 96.3 | 63.86 | 69.42 | 55 | 81.0 |
| $Na_2O$ and $K_2O$ | — | <.04 | 23.46 | 18.22 | 11 | 3.8 |
| CaO and MgO | — | — | 12.04 | 9.19 | — | 2 |
| $Al_2O_3$ and $Fe_2O_3$ | — | 0.4 | 1.30 | 2.71 | 1 | 2 |
| PbO | — | — | — | — | 33 | — |
| $B_2O_3$ | — | 2.9 | — | — | — | 13.0 |
| $As_2O_3$ | — | — | — | — | — | 0.002 |

**a. Quartz Glass.**—Pure fused quartz has already been mentioned.

In 1940 the Corning Glass Works announced a new variety of quartz glass which is nearly pure silica. This is manufactured by leaching pyrex-type glasses in acid, leaving a porous residue which is then contracted by firing. This heat treatment produces a shrinkage of 36 per cent in volume, giving a compact, clear glass not unlike quartz in properties. For example (Dem. 125), it may be plunged red-hot into ice-water without cracking. Under similar conditions Pyrex brand glass and soft glass usually crack. Vycor brand silica glass No. 709, whose composition is given in Table 100, absorbs light in the ultraviolet region below 2800 Angstroms; but a special glass, No. 791, with essentially the same composition, transmits shorter wave lengths, and is useful for photochemical research.

**b. Lime Glasses.**—These preponderate in tonnage and are

*Courtesy of the Corning Glass Works*

200-inch telescope glass being examined, for strains, with a polariscope.

produced by fusing a mixture of soda ash ($Na_2CO_3$) or "salt-cake" ($Na_2SO_4$) with quartz sand and slaked lime ($Ca(OH)_2$), limestone ($CaCO_3$), or dolomite ($CaCO_3$, $MgCO_3$):

$$Na_2CO_3 + CaCO_3 + 6SiO_2 \rightarrow Na_2O, CaO, 6SiO_2 + 2CO_2.$$

The formula $Na_2O$, $CaO$, $6SiO_2$ shows the composition of window glass, but does not mean that glass contains $Na_2O$ and $CaO$ as such. It is, however, a convenient way of representing an analysis: *e.g.*, $Na_2SiO_3 = Na_2O, SiO_2$. In the manufacture of cheap glass, "salt-cake" ($Na_2SO_4$) may be substituted for $Na_2CO_3$. Sodium-calcium glass may be softened readily by heat.

When $K_2CO_3$ is substituted for $Na_2CO_3$, the glass is more difficult to fuse.

**c. Borosilicate Glasses.**—These important glasses were first made commercially some fifty years ago, but were rapidly improved when the United States was cut off from tough Jena (German) glass in 1917. Boric oxide imparts to borosilicate glasses low expansion coefficient, high resistance to chemical attack, and favorable electrical properties. Such glasses are used for laboratory ware, household baking ware, insulators, thermometer bulbs, etc. Sodium-aluminum borosilicate glasses, such as Pyrex brand chemical glass No. 774, are very resistant to heat and shock.

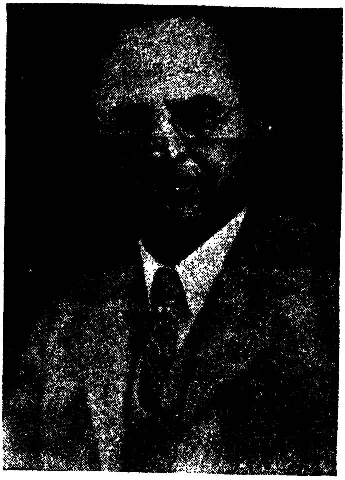
**d. Lead Glasses.**—Lead oxide is substituted for lime, and more or less potash for soda. The lead content is from 25 to 50 per cent, which often makes the glass nearly as heavy as iron (the density of ordinary glass is only 2.5 whereas glass containing 80 per cent lead is 6.33; cast iron is 7).

Lead glasses (flint glasses) on account of their high index of refraction are used for decorative ware, and because of their low electrical conductivity find application in tubing for leading-in wires in incandescent filament lamps.

**e. Special Glasses.**—During recent years many special glasses have been developed by intelligent research. Case-hardened glass for diving boards, glass building bricks (solid glass is 25 per cent harder to crush than cast iron), multicellular "bubble" glass which can be sawed and have nails driven into it, glass which shatters into a million smooth grains: these are a few new products. In addition there are plastic sheets, *which are not glass at all* since they contain no silicon; safety-glass, which is a sandwich of these plastic sheets between plate glass; and Polaroid glass which is similar to safety-glass save that organic crystals, iodoquinine sulfate, are imbedded in the plastic, these crystals having the property of passing only light which is vibrating in one particular plane.

Another variety has been popularly described as "invisible glass." By coating glass lenses with a thin film of magnesium or calcium fluoride (Cartwright) or of barium stearate (Fig. 157, Langmuir and Blodgett), or by etching off the oxide layer, reflection of light from the glass surface is reduced to a minimum. Motion picture camera and projection lenses so treated, the outer lenses etched and the inner lenses fluoride-coated, have stepped up screen illumination 30 per cent in 1940.

**f. Colored Glasses.**—In earliest times colored glass was used exclusively for decorative purposes; but today it also serves the useful purpose of absorbing certain deleterious wave-lengths of light, *e.g.*, amber bottles to prevent chemicals from photodecomposition, stop-and-go signals, sunglasses. These glasses are produced by adding traces of foreign salts.



*Courtesy of the General Electric Co.*

FIG. 157. Non-reflective glass (*center portion*) on a portrait of Dr. W. R. Whitney, Director of Research, the General Electric Company.

Cobalt oxide colors glass blue; chromium oxide or copper oxide, green; gold or copper, red, the exact hue depending upon the presence of sub-microscopic crystals of the metals in various glasses. The usual coloring material for red glass is selenium mixed with cadmium sulfide. Manganese dioxide colors glass violet; ferrous iron, green (bottle glass); ferric iron, yellow or brown. The green of ferrous iron is removed by manganese dioxide (glass-makers' soap). White, opal or milk glass is produced by cryolite, fluorite, bone ash, gypsum, feldspar, etc.

**479. Technology of Glass.**—Glass is a supercooled liquid which slowly, with the passage of centuries, crystallizes. The fact that it has a softening range, but no sharp melting point, permits it to be worked in the flame and blown into shapes. Ordinary glass has a softening range of 100–200°, whereas quartz has such a short range, about 50°, that one must be extremely dextrous in blowing quartz apparatus.

The batch of raw materials, including scrap glass (cullet), is fed into **melting pots** or tanks. The lining of these presents a problem in itself, being a silicate pot in which to melt silicates.

The molten glass is **removed** from the oven by several methods: for bulbs and tumblers it may be sucked out of the pot by automatic machines; for plate glass it is flowed continuously between rollers; and for pressed and blown ware, "gobs" of predetermined size are dipped up or sucked out by machinery.

Then comes the **blowing** operation. The mechanism of an automatic glass blowing machine is a marvel of engineering design: in the few seconds during which the glass is changing from a syrup to a solid the object must be blown and completely formed.

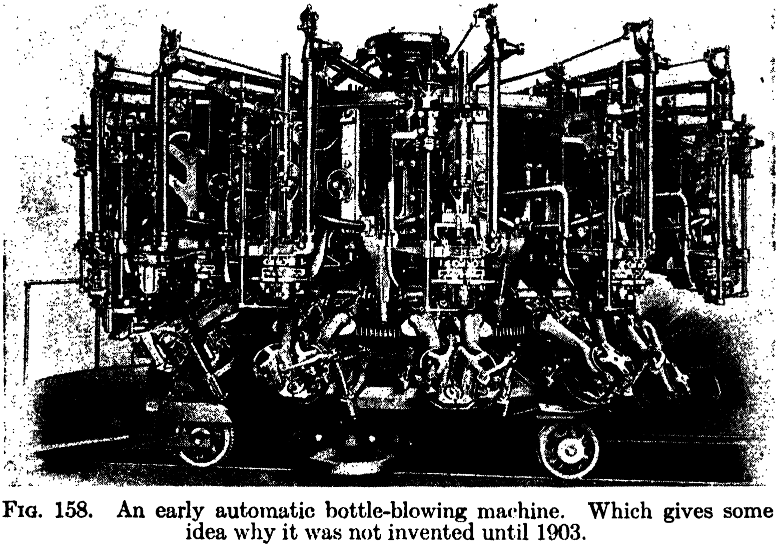


FIG. 158. An early automatic bottle-blowing machine. Which gives some idea why it was not invented until 1903.

The great automatic machines are almost lifelike in their performance, one machine doing the work of a very large number of men. Glass-blowing machines are a great boon, for tuberculosis has been the scourge of the glass-blower's trade; and the mortality in this branch of labor has been greatly reduced since the introduction of glass-blowing machines. The first fully automatic bottle-machine (Fig. 158) was invented in 1903 by J. Owens, an American. A single machine can produce 10,000 bottles per hour.

The primitive method of gathering on an iron pipe, shaping with hand tools, and blowing in a mold by means of the workman's breath is still used for ware made in small quantities.

Following the blowing, the strains in the glass are relieved by **annealing.** For some glasses this may require days or even months: for example, the giant 200-inch glass for the telescope at Mt. Palomar was held in an oven at 500° for fifty days to relieve internal strains, and then the temperature was lowered 1° every 30 hours for the next several months (page 517). Careful research has established the conditions for rapid annealing in mass operations, however, so that bottles, lamp bulbs, etc., are quickly annealed in specially developed *lehrs.* For instance, in the Corning Glass Company's soft-glass works in Pennsylvania and New York, which produce 85 per cent of the country's lamp bulbs, the raw materials entering the factory one day emerge as a million lamp bulbs within 24 hours.

**Finishing** the glassware consists in polishing, grading and so forth; or in frosting or etching with hydrofluoric acid (599, *c*).

High-grade optical glass for refracting lenses, telescopes and microscopes is melted in pots which are stirred to promote homogeneity and then removed from the furnace and cooled slowly. The chunks of glass thus obtained are softened into the shapes desired.

## QUESTION REVIEW

I. General. The non-metals (459). Boron and silicon (460).

1. Tabulate the non-metals according to Mendeléeff. Relate properties of these elements to their positions in the table.
2. How do boron and silicon differ from the other elements in their groups?

II. Boron and its compounds.

**a. Boron (461-463).**

3. Locate two sources of boron compounds.
4. Describe how boron is prepared. Give some of its physical and chemical properties.

**b. Boric acid (464).**

5. How is borax obtained? How would you "prospect" for boron compounds?

**c. Borax (465).**

6. How would you prepare $Na_2B_4O_7, 10H_2O$ from (a) kernite (b) colemanite (c) the pentahydrate?
7. Outline the industrial and laboratory uses for borax.

III. Silicon and its compounds.

**a. Silicon (466-468). Silicon halides (469).**

8. In what form is silicon prepared for use in the metallurgical industry? Give 4 equations showing chemical reactions of silicon.
9. Describe the chemistry of (*a*) smoke screen, (*b*) etching of glass.

**b. Oxy-compounds of silicon: silicon dioxide (470-471); fused quartz (472); silicic acids (473).**

10. Name and give the formulas of one silicate rock corresponding to each of the following: metasilicic, orthosilicic, trisilicic, and disilicic acid.
11. How are insoluble silicate rocks prepared for analysis of their metal content? Give equations.
12. Give a use for diatomaceous earth, clear fused quartz, hydrofluoric acid, water glass.
13. Explain how the tetrahedral arrangement in silicate minerals produces a variety of structures. Account for the fibrous nature of asbestos.

**c. Silicates: rocks (474-5); water glass (476); glasses (477–478).**

14. State the approximate compositions of Pyrex, Vycor, soft glass, hard glass, quartz glass, and lead glass. What differences in properties suits them to their particular uses?
15. Mention some recent glasses. Why are not clear plastics "glasses"? What is "invisible glass"?

**d. Technology of glass (479).**

16. Outline the steps in producing glass from the raw materials. The steps in fabricating a bottle. In fabricating a sheet of plate glass. In fabricating a lamp bulb. How long is glass annealed?

**Reading References:** Articles in the Appendix:

*Boron:* 18, 31, 35, 116, 206, 213 and 256.

*Ceramics:* 33, 71, 139 and 338.

*Glass:* 100, 105, 135, 214, 239, 252, 254, 255, 319 and 331.

*Silicon:* 102, 202 and 235.

# CHAPTER XXXIV

## CARBON AND ITS OXIDES. CARBIDES. CYANIDES

**480. Occurrence of Carbon.**—*Carbon* (Latin *carbo*, coal or charcoal) occurs in the free state in the form of the diamond and graphite. Carbon is a constituent of animal and vegetable tissues and of coal, petroleum, and natural gas. It may be regarded as the central element of the Organic Kingdom. Moreover, carbon is a constituent of all alcohols, animal and vegetable oils and fats, sugars, cellulose, ethers, etc. In combination with oxygen, it occurs in carbon dioxide, and very abundantly in carbonates, such as calcium carbonate (chalk, marble, and limestone) and magnesium carbonate. Carbon compounds are exceedingly numerous, over 400,000 being known.

Although carbon is widely distributed in the earth's crust, it is only a minor constituent of it,—about 0.19 per cent.

### THE DIAMOND

**481. Occurrence.**—The diamond has been used for ages as a precious stone. Originally it was obtained from the alluvial deposits in India; since 1727 the rich deposits of Brazil have been worked; and in 1867 the discovery of diamonds in the blue ground of South Africa opened up the rush which culminated in the powerful De Beers Consolidated Mines, controlled by Lord Cecil Rhodes, of scholarship fame. Today the Belgian Congo is the chief producer, having mined 7,201,000 metric carats of diamonds in 1939 as compared with South Africa 1,246,670 and Brazil 350,000. A metric carat is 0.2 g., the weight of the bean, or carat, of the locust tree, originally used in India in weighing diamonds.

Since diamond output, more than that of any other mineral product, comes from tropical countries the problem of tropical diseases becomes a mining problem.

The Belgian Congo also contributed a considerable quantity of industrial diamonds, imperfect samples unsuitable for jewelry, used as an abrasive and in drilling. There were 3,568,730 carats of industrial diamonds mined in 1939, worth $9,725,683 in comparison with 11,330,000 carats of jewels worth $39,270,000.

The origin of the diamond has always been a riddle, but it must have been formed at vast depths under great pressure. There is evidence to show that diamonds have crystallized out from a lava or magma which consists largely of magnesium silicates.

The history of some of the large diamonds is most interesting. The largest diamond ever found was the celebrated "Cullinan"; it was discovered in South Africa in 1905, and weighed in the rough state 3,032 carats (1.37 pounds avoirdupois). It was presented to King Edward the Seventh. The Pitt or Regent diamond is a magnificent colorless diamond which weighs 136¼ carats. It is in the Louvre (Paris). This stone was found by an Indian slave, who wandered to Madras, where he was murdered on board a ship, and the diamond sold for £1,000. In 1710 it was purchased by Thomas Pitt, grandfather of the Earl of Chatham, for £10,000; and in 1717 he sold it to the Duke of Orleans for £130,000. The Kohinoor diamond, one of the British crown jewels, weighs 106 carats. Its authentic history begins before the birth of Christ. The celebrated Hope diamond weighs 44¼ carats and has an exquisite blue color.

Nearly 25,000 experts are engaged in the **diamond cutting** industry. The surface of the stone is cleaved or sawed into many facets to increase its brilliancy; and the angle of the cut, the elimination of flaws, and getting the largest cut stone from a given specimen, are problems involving considerable skill. Formerly centered in Holland, the diamond cutting industry moved to Antwerp with the rise of mining in the Belgian Congo.

**Artificial Diamonds.**—From time to time the preparation of artificial diamonds by compressing carbon at high temperatures has been reported. Usually graphite or silicon carbide is formed. One of the first to report such an attempt was Moissan in 1893, who plunged sugar charcoal dissolved in molten iron into cold water. In 1940 Bridgeman at Harvard found that at the super-pressure of 3,500,000 pounds per square inch, graphite was not converted into diamond at room temperature.

**482. Properties.**—The diamond crystallizes in the isometric (regular) system. When the diamond is examined by means of

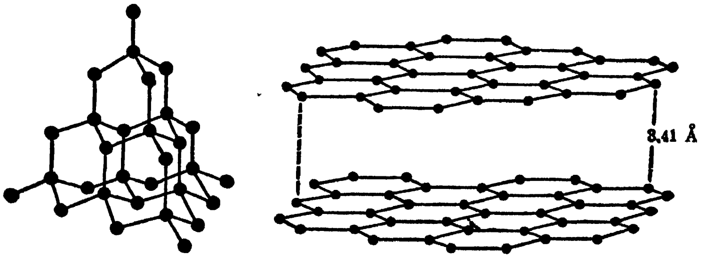


Fig. 159. Space lattices for allotropic forms of carbon.

X-rays (92) it is found to consist of atoms arranged as shown in Fig. 159. The carbon atoms are arranged in the form of tetrahedra, with four atoms at the corners and a fifth atom at the mass-center. The average sp. gr. is about 3.5, and it is the hardest substance known. It has a high index of refraction, and its property of scattering light to such a great extent renders it very valuable as a gem. The pure diamond is colorless and transparent, but is frequently colored by small quantities of impurities. Some of the blue, red, or green stones are as valuable as the colorless variety. The black variety (*carbonado* or *bort*) is of no value as a gem, but on account of its extreme hardness it is used for boring, cutting, and grinding. The diamond is very resistant to the action of most chemicals; it is not attacked by acids. When it is heated in the absence of air above 1,000°, it is transformed into a coke-like mass. When heated in air or oxygen to a high temperature, it burns to form carbon dioxide (Lavoisier, 1772). Davy (1814) proved that carbon dioxide is the sole product formed (excepting a very small amount of ash) when the diamond is burned.

## GRAPHITE

**483. Natural Graphite.**—*Graphite* (Greek, meaning *write*) was known to the ancients, but originally it was confused with the sulfide of molybdenum ($MoS_2$); hence both minerals were termed *plumbago*. Graphite occurs widely distributed in both a crystalline and an amorphous form.

Domestic consumption in 1913 was 21,500 tons of the crystalline and 6500 tons of the amorphous forms; but due to the decline in crucible-steel (430) and the rise in radio dry-batteries (198), the consumption was reversed in 1938 to 5700 and 12,100 respectively. Ceylon, chief producer in 1913, has been surpassed in production by Russia, Chosen and Bavaria. To the United States, Mexico supplies most of our amorphous graphite, and Madagascar and Canada the crystalline variety.

**484. Artificial Graphite.**—About 10,000 tons of graphite is manufactured each year by the Acheson process at Niagara Falls,

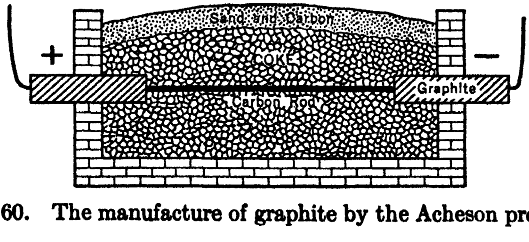


Fig. 160. The manufacture of graphite by the Acheson process.

where electricity is cheap. Amorphous carbon (anthracite coal or coke) is heated in an electric furnace in the presence of ferric oxide or silica. A carbon rod is used as a core between the terminals (Fig. 160). Carbides are first formed, but at the very high temperature attained (3,500° C.) these dissociate, yielding graphite, which is deposited as nearly pure carbon. The electrodes are made of graphite. The furnace is nearly filled with coarse grains of anthracite coal or coke. The charge is covered with a mixture of sand and carbon. Graphite also is formed when melted iron containing carbon in solution cools.

**485. Properties.**—Graphite is a soft, gray-black, shiny substance which feels greasy to the touch. Its density is about 2.3, and, unlike the diamond, it is a good conductor of heat and electricity. Graphite leaves a black mark when drawn across paper. It formerly was supposed to contain lead, hence the name black-lead or plumbago. Not many chemical reagents attack graphite appreciably. Even oxygen at a high temperature does not attack it readily.

The arrangement of the atoms of carbon in graphite is in the form of a hexagonal network, being quite different from that of the diamond; and this difference in structure accounts for the greasy, lubricating property of the former (Fig. 159).

**486. Uses.**—As intimated above, the important consumers of graphite have changed radically in the past quarter-century. Today it is used in fillers for dry cells, for foundry facings, as a lubricant, in painting iron, electrotypers' leads, stove and metal polish, glazing powder, polishing shot, etc. Artificial graphite can be used for practically any purpose to which natural graphite is put. It is particularly adapted to the manufacture of electrodes, and is largely utilized in the manufacture of lubricants, paints, etc.

Graphite in colloidal suspension in water (*aquadag*) or in oil (*oildag*) is used as a lubricant.

## "AMORPHOUS" CARBON

**487. Coke.**—Coke is produced on an enormous scale by subjecting soft coal to destructive distillation, or carbonization. A ton of coal yields approximately 1500 pounds of coke. The **by-product coke oven** is a brick chamber surrounded by heating flues and furnished with a pipe through which the valuable gases and coal-tar is led off. World production of coke amounted to 135,000,000 tons in 1938; of this Germany (32 per cent), the United States (21 per cent) and U.S.S.R. (15 per cent) were the chief producers.

Seventy per cent of the domestic coke in 1939 went into the blast furnaces for manufacturing pig iron (423); the remaining 30 per cent was consumed in foundries, in smelting nonferrous metals, in manufacturing water gas, and for domestic heating. Total consumption in the United States in 1939 was 44,953,082 tons of coke.

In addition to the by-product coke ovens, coke is also made (about 3 per cent of the total) in old-fashioned bee-hive ovens; also during the refining of petroleum, and by heating coal at low temperatures.

**Gas-carbon** is a hard, iron-grey carbon deposit formed in the upper portion of the retort during the distillation of coal; it is suitable for electrodes.

**Carbon-black** is formed by burning a flame in an insufficient supply of air; out of 280,000 tons produced in this country in 1939, 89 per cent went for compounding with rubber in automobile tires, the rest was used in printing inks and pigments.

**Lampblack** is a soot from the incomplete combustion of oil, and is used in printer's ink.

**488. Charcoal.**—The purest "amorphous" carbon is made by heating cane sugar, air being excluded:

$$C_{12}H_{22}O_{11} \rightarrow 12C + 11H_2O.$$

The charcoal is freed from mineral matter by boiling with acids, and is then ignited in a current of chlorine to remove the last traces of hydrogen. Charcoal is manufactured on a very large scale by heating wood in retorts; that is, the vegetable matter is subjected to destructive distillation (Fig. 161). Various volatile by-products, such as wood (methyl) alcohol, acetone, and acetic acid are obtained.

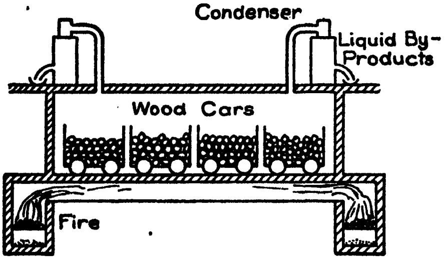


FIG. 161. The manufacture of charcoal from wood.

**Bone black or animal charcoal,** made by heating bones and animal refuse in iron retorts, is chiefly $Ca_3(PO_4)_2$ with a relatively small proportion of carbon. Its great decolorizing power makes it valuable in the purification of sugar.

**489. Physical Properties of Charcoal.**—X-ray analysis has shown that charcoal is more or less crystalline, like graphite, with a hexagonal network of carbon atoms.

Amorphous carbon melts at about 3500°. Although its density is 1.9, it floats in water owing to the fact that it contains absorbed air.

DEMONSTRATION 127. ABSORPTION BY CHARCOAL

Materials: (*a*) Condenser tube packed with charcoal and clamped upright, solutions of indigo, brown sugar; (*b*) thistle tube leading into a 4 oz. bottle filled with activated charcoal, from which a delivery tube runs to a pneumatic trough of water; five 4 oz. bottles; (*c*) illuminating gas bubbling through 10 cc. of benzene in a 250 cc. washing cylinder and thence through two outlets, one a nozzle, the other a tube of activated C and nozzle; (*d*) 2-liter stoppered flask containing a few drops of bromine, activated charcoal.

The absorptive properties of charcoal are readily demonstrated. (*a*) Indigo or sugar solutions are decolorized by filtering through charcoal. (*b*) Upon filling the bottle with water, all five 4 oz. bottles can be filled with expelled air. (*c*) Illuminating gas bubbled through benzene burns with a smoky flame; if run through activated charcoal the benzene is absorbed and the flame is blue. (*d*) A little activated charcoal quickly absorbs the bromine vapor. These absorbing properties are greatly dependent upon the source of the charcoal, and whether it is in an activated state. **Charcoal** for gas masks, for instance, is prepared from cocoanut or other shells, and is activated by reheating the charcoal in steam or air. A single cubic inch of this may have an active area of several acres. The absorptive property of charcoal makes it useful as a catalyst, as a catalyst supporter, and in liquid air traps containing charcoal for freeing highly evacuated systems of the last traces of gaseous impurities.

**490. Chemical Properties of Carbon.**—At ordinary temperatures carbon is not a reactive substance. Graphite appears to be the most stable form, for at very high temperatures other forms of carbon are changed to graphite. When carbon is heated in air or oxygen it burns to form carbon dioxide with the liberation of energy:

$$C + O_2 \rightarrow CO_2 + 94{,}400 \text{ cals.}$$

In a limited supply of oxygen, carbon monoxide is also formed. At high temperatures it combines with sulfur to form carbon disulfide ($CS_2$), and with silicon and with certain metals to form

**carbides:** *e.g.*, $SiC$, $CaC_2$ and $Al_4C_3$. M. Berthelot showed that carbon unites directly with hydrogen to form acetylene ($C_2H_2$) when an electric arc is passed between carbon poles surrounded by hydrogen. It also combines with iron to form a carbide ($Fe_3C$).

Carbon, at high temperatures, is an excellent reducing agent. Enormous quantities of it are used in metallurgical operations, such as the reduction of oxides of iron and of zinc.

### CARBON DIOXIDE, $CO_2$

**491. History.**—van Helmont, in the seventeenth century, was the first to distinguish between carbon dioxide and ordinary air. Joseph Black (1754) showed that carbon dioxide could be obtained by heating such compounds as the carbonates of calcium and magnesium, and that it was absorbed by alkalies; hence it was called by him "fixed air." Black's investigation of *magnesia alba* ($MgCO_3$) was a milestone of chemical research. Among other things he proved that upon heating magnesium carbonate it decomposes into carbon dioxide and magnesium oxide (*magnesia usta*).

**492. Occurrence.**—Carbon dioxide occurs in the air, in natural waters, and in the soil; it escapes through vents and fissures in the earth's crust in certain localities: *e.g.*, the Poison Valley in Java and the *Grotta del Cane* near Naples. According to Mendeléeff, there is a depression near the Rhine, in the neighborhood of extinct volcanoes, which is constantly filled with carbon dioxide.

> "The insects which fly to this place perish. . . . The birds chasing the insects also die, and this is turned to profit by the local peasantry."

The carbon dioxide found in nature comes from a number of different sources, such as combustion, decay, fermentation, respiration, and the decomposition of carbonates. Vast quantities of the carbonate of calcium (limestone, marble, chalk, etc.) and of magnesium carbonate also occur in nature. *Dolomite* is magnesium limestone ($CaCO_3$, $MgCO_3$). Other carbonates such as *siderite* ($FeCO_3$), *smithsonite* ($ZnCO_3$), and *witherite* ($BaCO_3$) are fairly abundant.

**493. Preparation.**—(*a*) Carbon dioxide is produced chiefly as a by-product from the flue gases from coking ovens. The gases at high pressures are scrubbed through washing soda, which forms a solution of the bicarbonate and allows nitrogen, carbon monoxide and other gases to escape. Upon reducing the pressure and heating, the reaction is reversed and the carbon dioxide is regained:

$$CO_2 + Na_2CO_3 + H_2O \underset{\text{hot}}{\overset{\text{cold}}{\rightleftarrows}} 2NaHCO_3.$$

The escaping carbon dioxide is washed and then stored in cylinders under a pressure of about 1,100 pounds per sq. in., or sold as "Dry Ice." The $Na_2CO_3$ may be used over again.

(*b*) The gas is also obtained from limestone kilns, a reaction which is driven to the right by allowing $CO_2$ to escape:

$$CaCO_3 \rightarrow CaO + CO_2.$$

In one plant at Pittsburgh 8 tons of low-grade stone yield 3 tons of gas and 4¾ tons of lime.

(*c*) A small quantity of carbon dioxide is obtained from natural fissures in the ground in Mexico and southwestern United States.

(*d*) Another lesser source is the brewing industry where $CO_2$ is a product of the fermentation of glucose:

$$\underset{\text{gluclose}}{C_6H_{12}O_6} \rightarrow \underset{\text{alcohol}}{2C_2H_5OH} + 2CO_2 \uparrow.$$

Each of the foregoing methods is used in some locality or another. Because of the perishable nature of "Dry Ice" it is usually generated for local consumption; and since $CO_2$ is merely a by-product of a number of important industries, the method by which it is obtained is largely a matter of geography and local industries.

**Carbon dioxide is formed** when organic matter is burned, during respiration in the bodies of animals, during the decay of vegetable and animal matter, from the reduction of oxide ores with carbon, and upon treating a carbonate with acid. (Write equations for these.)

The latter is a laboratory method; but tanks of the gas are so commonplace today that the chemist seldom resorts to any other source.

**494. Physical Properties.**—Carbon dioxide is a colorless gas 1.529 times heavier than air. It sublimes, *i.e.*, the vapor pressure of the solid is so great that it evaporates without melting. Nearly twice as much of it dissolves at 0° (1.8 vols. in 1 vol of water at 760 mm.) as at 15°, a factor of some importance in the soda-water business. Soda-water usually contains the gas under 3–4 atmospheres pressure, and effervesces as the $CO_2$ escapes into the air.

Tank $CO_2$ is liquid; and if this liquid is allowed to escape by elevating the bottom of the tank, the first portion of the liquid which evaporates absorbs so much heat that the rest of the liquid forms **dry ice,** a crystalline snow-like solid. Solid $CO_2$ should not be pressed against the skin since it causes painful blisters, like burns.

### DEMONSTRATION 128. MERCURY HAMMER WITH DRY ICE

Materials: Small board, carpet tacks, hammer handle clamped with its head immersed in Hg in a 1 × 3″ paper box 1″ deep, set in a 10 cm. crystallizing dish, acetone, 4″ square of Dry Ice.

A slush of Dry Ice in acetone is used in research as a freezing mixture ($-100°$ to $-80°$). When poured upon the mercury it quickly solidifies into a mercury hammer with which, after peeling off the box, tacks may be driven into a board.

Eight per cent of $CO_2$ in the air is poisonous, but lesser quantities are not particularly dangerous; in this respect carbon dioxide differs markedly from carbon monoxide (**502**).

**495. Chemical Properties.**—Carbon dioxide is a very stable compound even at 2000°. The equilibrium which it establishes with the CO in the blast furnace has already been referred to:

$$2C + O_2 \rightarrow 2CO; \qquad 2CO + O_2 \rightleftarrows 2CO_2.$$

### DEMONSTRATION 129. CHEMICAL PROPERTIES OF $CO_2$

Materials: Tube of limewater, straws, limestone, HCl, test-tube.

Carbon dioxide combines readily with oxides or hydroxides of active metals forming carbonates; and in the presence of excess $CO_2$, bicarbonates are formed:

$$CaO + CO_2 \rightarrow CaCO_3.$$

$$\underset{\substack{\text{Limewater}\\ \text{(clear)}}}{Ca(OH)_2} \xrightarrow{+CO_2} \underset{\text{(milky)}}{CaCO_3} \downarrow \underset{\text{heat}}{\overset{+CO_2+H_2O}{\rightleftarrows}} \underset{\substack{\text{bicarbonate}\\ \text{(clear)}}}{Ca(HCO_3)_2}.$$

Upon breathing into limewater a milky precipitate forms (there is 4 per cent of $CO_2$ in exhaled breath); after a few minutes the precipitate redissolves as a soluble bicarbonate. Upon heating the solution the carbonate is again precipitated.

**496. Uses.—Dry Ice** is a familiar form of solid $CO_2$ obtained by the rapid evaporation of liquid $CO_2$ into steel molds; it is pressed into blocks a foot square, and used as a food refrigerant.

Freight cars often cannot use Dry Ice since it becomes powdery in less than a week, making it unsuitable for cross-country hauling.

In 1939 production of Dry Ice reached 156,609 tons valued at $4,618,937, an all-time high. The ice-cream industry was the principal customer, although the use of frozen foods continued to expand. Liquid and gaseous carbon dioxide valued at $4,939,508 (50,358 tons) was consumed by the beverage industry. Half a million tons of carbon dioxide is also needed each year in the washing soda and baking soda industries.

### DEMONSTRATION 130. $CO_2$ AS A FIRE EXTINGUISHER

Materials: (*a*) Balance counterpoising two 1-liter beakers; 1-liter beaker; (*b*) large jar filled with $CO_2$, 30 cm. of 6 mm. tubing, bubble-soap; (*c*) candles on a series of steps leading down into a glass trough 6″ wide × 3′ long × 2′ deep, a candle on each step; tall cylinder of $CO_2$; (*d*) 100 g. $Al_2(SO_4)_3$ in 500 cc. water; 10 g. licorice in 500 cc. hot water plus 50 g. $NaHCO_3$ added slowly; tall cylinder.

That $CO_2$ is heavier than air may be demonstrated by (*a*) pouring it into a beaker on the balance, (*b*) blowing a soap-bubble of air and "floating" it in the jar of $CO_2$. The jar may be carried around with the bubble in it.

The extension of this property in the use of $CO_2$ in fire-extinguishers is shown (*c*) by pouring $CO_2$ down the steps, the lower candle being extinguished first, and (*d*) by mixing the two "foamite" solutions. Foamite is an extinguisher used for gasoline fires, this foam being kept in suspension by the licorice. Modern fire extinguishers are merely tanks of liquid $CO_2$ which spray out $CO_2$ gas over the fire (Fig. 162). Another extinguisher, upon inverting, mixes $H_2SO_4$ and a solution of $NaHCO_3$, forming up to 125 pounds pressure of $CO_2$ (equation?), which forces a jet of water upon the fire.

$CO_2$ is important in making dough rise (**305**).

**497. The Oxygen-Carbon Dioxide Cycle.**—This important life cycle has been previously discussed (**271**). Plants assimilate water and carbon dioxide, and give off oxygen; animals assimilate oxygen and carbohydrates and give off water and carbon dioxide. Carbon dioxide is thus an important plant food.

**498. Carbonic Acid and Carbonates.**—As a typical non-metal, carbon forms an oxide which dissolves in water to give an acid:

$$H_2O + CO_2 \rightleftarrows H_2CO_3.$$

For this reason $CO_2$ has, in the past, been referred to as *carbonic* *acid gas*, or *carbonic anhydride*. It is one of the feeblest of acids, and has never been obtained excepting in solution.

Two salts are formed: the **carbonates** and the **bicarbonates.** With these we should already be familiar, *i.e.*, $Na_2CO_3$, $10H_2O$, washing soda and $NaHCO_3$, baking soda; $CaCO_3$ and $Ca(HCO_3)_2$ etc.

*Courtesy of Walter Kidde & Company*

FIG. 162. Fire-fighting with carbon dioxide.

The behavior of limestone in the presence of natural waters containing carbon dioxide makes it easy to understand the formation of caves, such as the Mammoth Cave in Kentucky (page 535). On account of the slow action of carbonic acid, soluble calcium bicarbonate is formed (see Hard Waters, 349), and in the course of time much of the rock is eaten away, leaving a cave. When the solution loses carbon dioxide at the roof of the cave, calcium carbonate is left behind as a sort of stony icicle called **stalactite**; but when drops of water fall to the bottom of the cave, evaporation occurs with further loss of carbon dioxide, and deposits of calcium carbonate are formed which are known as **stalagmites.**

*Courtesy of the Luray Caverns Corporation (Va.)* →

The stalactites and stalagmites may unite, forming pillars or columns. A limestone cave therefore has a tendency to refill itself.

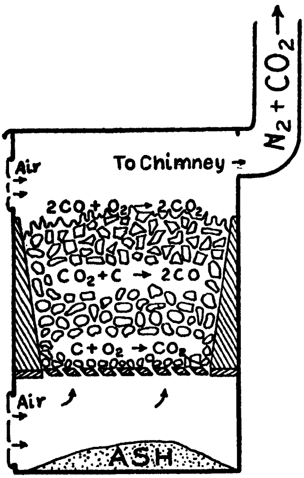

$N_2 + CO_2$
Air
To Chimney
$2CO + O_2 \rightarrow 2CO_2$
$CO_2 + C \rightarrow 2CO$
$C + O_2 \rightarrow CO_2$
Air
ASH

FIG. 163. Formation of the oxides of carbon in a coal stove.

In Kents Cavern, near Torquay, England, stalagmites are being built up at the rate of one inch in 1,000 years. One stalagmite in this cavern is 4.5 feet in height, and the period of its formation is probably over 50,000 years.

### CARBON MONOXIDE, CO

**499. Preparation.**—Carbon monoxide is formed in an ordinary grate fire from the combination of carbon dioxide with heated carbon (Fig. 163):

$$CO_2 + C \rightarrow 2CO.$$

Incomplete combustion in stoves and furnaces, and in an automobile engine also forms carbon monoxide. Since the gas is highly poisonous, an automobile should not be operated in a closed garage.

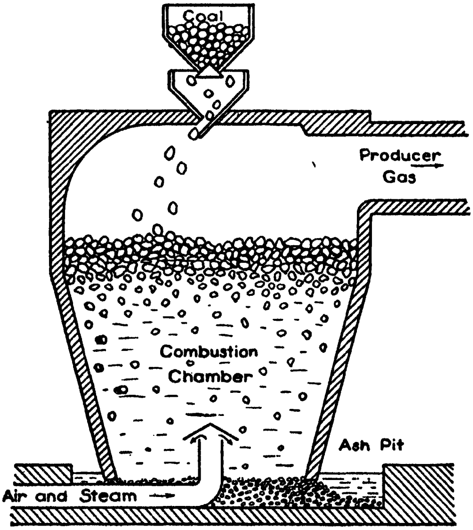


FIG. 164. The manufacture of producer gas.

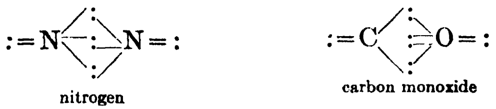
In the laboratory carbon monoxide may be prepared conveniently by treating formic acid, $HCOOH$, or oxalic acid, $(COOH)_2$, with concentrated sulfuric acid. The acids are heated, and the sulfuric acid abstracts water. In the case of oxalic acid, carbon dioxide is also formed and must be removed by passing the gas through a solution of alkali.

$$HCOOH \rightarrow CO + H_2O,$$
$$(COOH)_2 \rightarrow CO + CO_2 + H_2O.$$

**By far the most important gases containing carbon monoxide are**

**water gas:** $C + H_2O \rightarrow CO + H_2.$
**producer gas:** $C + \text{air} \rightarrow 39\%\ CO + 60\%\ N_2.$ **(Fig. 164.)**

**500. Physical Properties.**—Carbon monoxide is a colorless gas and practically odorless and tasteless. The gas is only very slightly soluble in water and is difficult to liquefy. It has the same electronic arrangement as nitrogen (Fig. 165),


nitrogen

carbon monoxide

FIG. 165. Electronic structures.

and resembles it closely in physical properties as shown in Table 101.

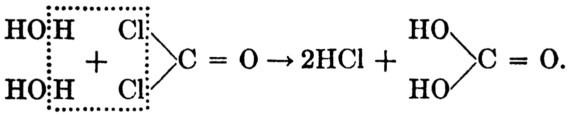
TABLE 101. PHYSICAL PROPERTIES OF NITROGEN AND OF CARBON MONOXIDE

| | Mol. Wt. | Sp. Gr. (air) | C.P. | C.T. | B.P. | M.P. |
|---|---|---|---|---|---|---|
| $N_2$ | 28 | 0.967 | 33.5 atmos. | −147° | −195.5° | −210.5° |
| $CO$ | 28 | 0.967 | 35.5 atmos. | −139.5° | −190.0° | −211.0° |

**501. Chemical Properties.**—Carbon monoxide is an unsaturated compound, and as such has a tendency to combine with other substances to give carbon a valence of 4. Thus CO combines with oxygen to form carbon dioxide; with members of the iron family to form carbonyls, $Ni(CO)_4$ and $Fe(CO)_4$; and in sunlight with $Cl_2$ to form **phosgene** (Greek, *generated by light*) or **carbonyl chloride:**

$$CO + Cl_2 \xrightarrow[\text{C catalyst}]{\text{light or}} COCl_2 \text{ (phosgene)}$$

Phosgene is a colorless liquid used in the production of dyes. Since it has a low boiling point (8°) and its vapor is very poisonous, it is used extensively as a war gas. When inspired, the phosgene hydrolyzes in the lungs and forms HCl:



$$\begin{matrix} HO \vdots H \\ HO \vdots H \end{matrix} + \begin{matrix} Cl \\ Cl \end{matrix} \!>\! C = O \rightarrow 2HCl + \begin{matrix} HO \\ HO \end{matrix} \!>\! C = O.$$

In the blast furnace and in other metallurgical processes CO is a reducing agent of particular effectiveness since, as a gas, it comes into intimate contact with the oxide ore,

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2.$$

Carbon monoxide is readily absorbed by an ammoniacal or hydrochloric acid solution of cuprous chloride, a fact of importance in gas analysis.

**502. Physiological Action.**—Carbon monoxide is a very poisonous gas; it unites with the hemoglobin of the blood corpuscles to form **carbonyl-hemoglobin**, a stable compound, which shuts off the supply of oxygen. One vol. of CO to about 800 vols. of air will produce death in about 30 minutes, and 1 vol. in 100,000 vols. of air produces symptoms of poisoning. Birds and mice are more sensitive to its action than is man.

## ELECTRIC FURNACE PRODUCTS

**503. Electrochemical Industries.**—With electricity growing ever cheaper, electrolysis has been used with water solutions to prepare oxygen, hydrogen and chlorine, and to refine metals such as copper, silver and gold; and electrolysis of fused salts gives us aluminum, sodium and the alkali metals, calcium and the alkaline earth metals, and chlorine. Still another type of electrical apparatus is the **electric furnace**. Moissan invented it fifty years ago. Electric furnace steel has displaced crucible steel.

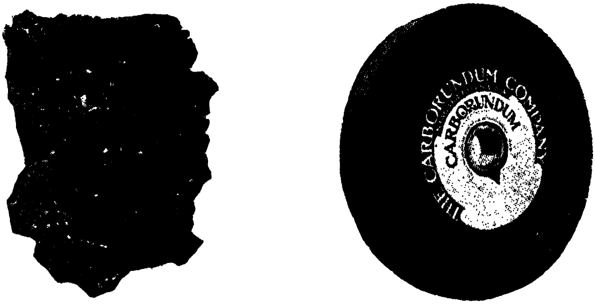
Carbon can be caused to combine with a number of materials, solids or vapors, by piling coke or charcoal around graphite electrodes in a brick oven, and passing enormous currents. As may be surmised, the electrochemical industries have congregated at Niagara Falls. Lately the enormous hydroelectric power in other parts of the country is being utilized, particularly in isolated sections where electricity cannot find any other market. In the electric furnace, carbon combines directly with sulfur vapor to form carbon disulfide, $CS_2$; with pulverized lime to form calcium carbide, $CaC_2$; and with sand, to which a little salt and sawdust have been added, to form silicon carbide, SiC:

$$\begin{aligned} C + 2S &\rightarrow CS_2 \text{ (liquid)}, \\ 3C + CaO &\rightarrow CO + CaC_2, \\ 3C + SiO_2 &\rightarrow 2CO + SiC. \end{aligned}$$

**504. Calcium Carbide.**—Commercial calcium carbide is a hard, brittle, dark-gray, crystalline mass. When pure, it is quite colorless and transparent. It reacts with cold water with great readiness, forming **acetylene, $C_2H_2$:**

$$CaC_2 + 2HOH \rightarrow Ca(OH)_2 + C_2H_2.$$

Of recent years this reaction has assumed an important rôle in our synthetic chemistry for it is the starting point for Buna rubber in Germany, and Neoprene rubber by duPont; and numerous plastics and synthetic fibers, such as the vinyl compounds, are manufactured from acetylene. At high temperatures nitrogen combines with calcium carbide to form **calcium cyanamide,** $CaCN_2$; this was once an important fertilizer, but today it has been supplanted by fertilizers made from synthetic ammonia (512). Cyanamide's modern importance relates to the formation of resins from **melamine,** a ring compound formed from three cyanamide units.



*Courtesy of the Carborundum Company*

FIG. 166. Silicon carbide and its use as an abrasive.

**505. Silicon Carbide.**—About 50,000 tons of silicon carbide for abrasives is made by the Acheson process at Niagara Falls each year. The crystals often have a beautiful, iridescent luster, but they may vary from black to green, to practically colorless. It is extremely hard, being harder than corundum (Fig. 166).

Silicon carbide is decomposed at 2,200°, is stable in the air, is not attacked by acids, but is decomposed by fusion with caustic alkalies.

**506. Carbon Disulfide.**—Carbon disulfide is a liquid boiling at 46°. It has a disagreeable odor, a high index of refraction, a density of 1.292; and it is slightly soluble in water. It must be handled with care since it is both poisonous and very inflammable (kindling temperature under 200°).

Enormous quantities of carbon disulfide are consumed in "ripening" wood-pulp (cellulose xanthate) in the viscose process for rayon (655). $CS_2$ is also a solvent for fats, resins, rubber, sulfur and iodine. It is used for exterminating burrowing animals such as the gopher or rat.

**507. Other Carbon Compounds.**—(Not electric furnace.) When carbon disulfide is heated with dry chlorine, with a trace of iodine catalyst, **carbon tetrachloride** is formed (also sulfur monochloride ($SCl_2$)). Carbon tetrachloride mixed with gasoline or benzene is a solvent for grease in dry-cleaning establishments. $CCl_4$ is sold as a fire extinguisher (**Pyrene**); for this purpose it may be mixed with an equal quantity of trichloroethylene $CHCl : CCl_2$. The vapors are heavy and form a blanket over the fire, cutting off the oxygen supply.

Another important class of carbon compounds contains the **cyanide radical** (**CN**). Most of them are poisonous. Thus **cyanogen** $C_2N_2$ is a deadly gas; **prussic acid** (hydrocyannic acid) HCN is a poisonous liquid boiling at 26°; KCN and NaCN are poisonous solids used in the metallurgy of silver and gold, and in electroplating (329). Also **cyanates** and **thiocyanates** are well known. Potassium thiocyanate, KCNS, is used in detecting ferric and cobaltous ions (446).

## QUESTION REVIEW

I. CARBON (480).

**a. Diamond (481-482). Graphite (483-486). Amorphous (487-489).**

1. Where are the diamond fields of the world located?
2. Where does the United States get its natural graphite? its artificial graphite?
3. What properties of graphite adopt it to its uses?
4. How many tons of coal (488-489) are required to give the tonnage of coke consumed annually in the United States? How much iron ore, containing 50 per cent iron, will this reduce?
5. Give a use for carbon black, lampblack, cocoanut shell charcoal, bone black, activated charcoal.
6. Describe some experiments illustrating the properties of activated carbon.

**b. Chemical properties of carbon (490).**

II. CARBON DIOXIDE.

**a. History (491). Occurrence (492). Preparation (493).**

7. Outline three industrial sources of carbon dioxide. By which method would it probably be obtained in (*a*) Pittsburgh, (*b*) Milwaukee, (*c*) Mexico?

**b. Properties (494-495). Uses (496).**

8. State two important physical properties of carbon dioxide which are utilized industrially.
9. Explain, giving equations, everything that occurs when one breathes into limewater, and then heats the final product. Of what significance are these reactions in (*a*) the production of $CO_2$ from flue gases (*b*) the formation of limestone caves (*c*) softening temporarily hard waters?

**c. The carbon dioxide-oxygen cycle (497).**

10. Show the equations involved in the cycle.

**d. Carbonic acid and the carbonates (498).**

III. CARBON MONOXIDE. Preparation (499). Properties (500-502).

11. Explain, giving equations, the reactions in an ordinary grate-fire. What causes the blue flame? Why do automobiles give out CO?

12. Write the formula for producer gas. For water gas.
13. Discuss the combination of CO with $Cl_2$. With $N_2$. With hemoglobin.

IV. ELECTRIC FURNACE PRODUCTS (503). Calcium carbide (504). Silicon carbide (505). Carbon disulfide (506).

14. Write the equations for the formation of these three compounds.
15. State the chief use of each of these compounds.

V. OTHER CARBON COMPOUNDS (507).

16. Give the formula and a use for carbon tetrachloride, prussic acid, sodium cyanide, a cyanate, a thiocyanate.

**Reading References:** Articles in the Appendix:

*Carbon:* 62, 126, 132, 202, 314, 320 and 407.

*Carbonates and oxides of carbon:* 22, 36, 57, 113, 211, 320, 325 and 407.

*Other carbon compounds:* 20, 36, 102, 150, 153, 235, 301 and 407.

# CHAPTER XXXV

# NITROGEN AND AMMONIA

### NITROGEN $^{14.008}_{7}N$

**508. Importance and Occurrence.**—Although most animals and plants do not assimilate nitrogen directly from the air, nitrogen eventually finds its way into living matter in the form of **proteins** which contain the amine ($NH_2$) radical. It is therefore essential to life; and a bountiful harvest and vigorous growth of grass, flowers and trees is dependent upon proper nitrogenous fertilizers.

Constituting four-fifths of the air by volume, nitrogen is present in the free state in enormous quantity. There are, for instance, about 20,000,000 tons of nitrogen above each square mile of the earth's surface.

The greater abundance of free nitrogen is due to its inertness under ordinary conditions and to the further fact that many nitrogen compounds are unstable and therefore tend to give up nitrogen to the atmosphere. Moreover, nitrates, ammonia, and certain other nitrogen compounds are soluble in water and accordingly do not enter into the composition of the outer crust of the earth as do many compounds containing such elements as oxygen, silicon, calcium, aluminum, and iron. Clay, or aluminum silicate, for instance, is insoluble and very abundant.

Nitrogen is also an essential constituent of all commercial explosives, such as guncotton and trinitrotoluene (T.N.T.), as well as of valuable fertilizers, such as Chile saltpeter and ammonium sulfate; also of nitric acid, ammonia, certain useful drugs, medicines, and dyes.

**509. History and Preparation.**—Dr. D. Rutherford, Professor of Botany in the University of Edinburgh, in the year 1772 recognized nitrogen as a distinct substance. He introduced animals into closed vessels, and then absorbed the carbon dioxide ("fixed air") in caustic potash. The residual gas failed to support the life of animals and it extinguished a burning candle. Nitrogen was first found to be a simple substance by Lavoisier, who named it *azote*, the name still used by the French. Chaptal (1823) suggested the name **nitrogen** (Greek, *saltpeter* + *to produce*), because it is a constituent of saltpeter.

Nitrogen is obtained from liquid air: the more volatile nitrogen (B.P. −195.8°) passes off first, leaving the oxygen (B.P. −183°) behind. For research, this commercial nitrogen is passed over heated copper to remove traces of oxygen.

Nitrogen may also be prepared by removing the oxygen of the air by passing air over hot copper. Cupric oxide is formed which may be reduced by hydrogen or natural gas, and then used again. Nitrogen thus prepared is not pure, for it contains argon and smaller amounts of other gases. Phosphorus may also be used to remove oxygen from the air.

Nitrogen may likewise be prepared by heating ammonium nitrite:

$$NH_4NO_2 \rightarrow 2H_2O + N_2.$$

Since this salt is both expensive and unstable, the same reaction is brought about by heating a mixture of ammonium chloride and sodium nitrite.

**510. Physical Properties.**—Nitrogen is a colorless, tasteless, odorless gas, which is only slightly soluble in water. It may be converted into a colorless liquid and a white solid. The C.T. is −147° and the C.P. is 33.5 atmos. The liquid boils at −195.8°, and the solid melts at −209.9°. The sp. gr. of nitrogen (air = 1) is 0.96717, and the weight of 1 liter is 1.2507 g. (Leduc).

**511. Chemical Properties.**—Under ordinary conditions nitrogen is quite inactive; that is why it occurs so abundantly in the free state.

At high temperatures (Demonstration 104, section 340) it combines directly with certain elements to form **nitrides,** such as $Mg_3N_2$, $Li_3N$ and BN:

$$3Mg + N_2 \rightarrow Mg_3N_2.$$

It unites directly with oxygen in a spark (Arc process, **529,** *c*) and over a catalyst with hydrogen (Haber process, **514,** *b*). **Leguminous plants** (peas, clover, soy, etc.) assimilate atmospheric nitrogen by virtue of certain bacteria which live in the nodules on their roots. Nitrogen also combines with hot calcium carbide to form calcium cyanamide (**504**).

*The important Nitrogen Cycle has already been treated* (**272**).

**512. The Fixation of Nitrogen.**—The term **fixation of nitrogen** refers to making nitrogen in the air available to the plants. Nitrogen in the air is returned to the impoverished soil by a number of natural means (the nitrogen cycle).

Arrhenius estimated that 400,000,000 tons of fixed nitrogen fall annually into the earth and sea as the result of electrical action. Nitrogen thus fixed is a valuable source of nitrogenous food for growing plants. In addition, increasing quantities of artificial fertilizers are being added by man; this is strikingly illustrated in Table 102. This increase has taken place chiefly in Europe and Japan, in an effort to increase home production and to avoid the necessity of importing foodstuffs.

The common **artificial fertilizers** are ammonium sulfate, cyanamide, and calcium nitrate; these accounted for 35 per cent, 14 per cent and 8 per cent respectively of nitrogenous fertilizers in 1940. Ammonium nitrate is also used. These fertilizers are prepared by three processes. I. Fixation of nitrogen in the air involves the formation of ammonia from its elements (Haber, **514**, *b*), and subsequent conversion into nitric acid (Ostwald, **529**, *b*). II. Formation of coke from coal gives ammonia gas which may be caught in acid (**514**, *b*). III. Chile saltpeter, $NaNO_3$ (**529**, *a*), is a natural fertilizer which is claimed to be superior to the synthetic product. Table 103 indicates the relative importance of these three methods.

TABLE 102. WORLD USE OF NITROGENOUS FERTILIZERS

| Year | Tons of Nitrogen |
|---|---|
| 1913 | 55,000 |
| 1917 | 375,000 |
| 1925 | 600,000 |
| 1933 | 1,300,000 |
| 1938 | 2,492,000 |

TABLE 103. SOURCE OF NITROGEN

| | |
|---|---|
| Atmosphere (Haber) | 2,196,000 |
| By-product coke | 411,000 |
| Chile saltpeter | 224,000 |
| WORLD PRODUCTION 1937–1938 | 2,880,000 |

Of the 2,880,000 tons 86.8 per cent went for fertilizer; the remainder was used for explosives and other industrial products. The quantity 2,196,000 tons for atmospheric nitrogen represents only 53 per cent of the actual world capacity, which is estimated to be 4,100,000 tons. The Luena works in Germany alone have a capacity of 860,000 tons.

## AMMONIA, $NH_3$

**513. History.**—The early alchemists were acquainted with the formation of ammonia by the destructive distillation of animal refuse, such as bones, hoofs, and horns. The old name for ammonia, "spirits of hartshorn," attests this fact. Priestley (1774) discovered $NH_3$ gas; Berthollet (1785) determined its composition; and Faraday (1823) liquefied it.

### 514. Preparation and Manufacture of Ammonia.

**a. Laboratory Method.** Tank ammonia may be used. Otherwise, it is prepared by treating an ammonium salt with a strong base such as slaked lime (calcium hydroxide):

$$Ca(OH)_2 + \underset{\text{Ammonium sulfate}}{(NH_4)_2SO_4} \rightarrow CaSO_4 + 2NH_4OH \rightleftarrows 2NH_3 + 2H_2O.$$

The gas can be expelled by heat and collected by the downward displacement of air; it is dried by passing it through a tower containing quicklime.

**b. Haber Process (with variations).** Ammonia is manufactured by passing a mixture of hydrogen and nitrogen over a catalyst at 500–1000° and at 150 to 2000 atmospheres pressure:

$$N_2 + 3H_2 \rightarrow 2NH_3 + 21{,}880 \text{ cals.}$$

This is the process invented by the German, Fritz Haber, and developed industrially by Carl Bosch; because of this, Germany was able to carry on the war in 1914–18, making her explosives from the air.

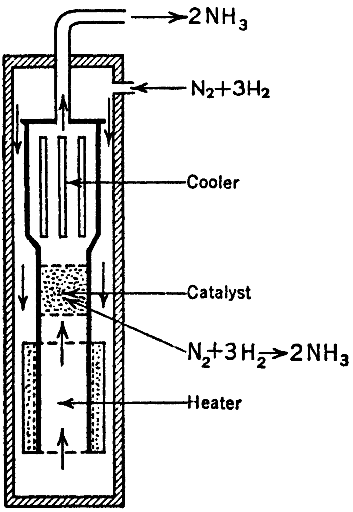


FIG. 167. Catalyst unit for the Haber process.

(1) *The reactants.* The **nitrogen** and **hydrogen** are prepared from a sort of producer and water gas respectively (**499**):

$$C + \text{air} \rightarrow 40\%\ CO + 60\%\ N_2,$$
$$C + H_2O \rightarrow CO + H_2.$$

Most of the CO is removed by treating with an excess of steam to form $CO_2$, which may be scrubbed out, and $H_2$ which is useful in the ammonia synthesis:

$$CO + H_2O \xrightarrow{\text{catalyst}} CO_2 + H_2.$$

The $CO_2$ is scrubbed out, leaving a mixture of $N_2$, $H_2$, and from 2 to 5 per cent residual CO. This latter must be removed, since it poisons the ammonia catalyst. To do this, the mixture is passed over a suitable catalyst to yield methyl alcohol (methanol), a valuable product:

$$CO + 2H_2 \xrightarrow{\text{catalyst}} \underset{\text{methanol}}{CH_3OH}.$$

The pure nitrogen and hydrogen are dried before being admitted to the chamber containing the ammonia catalyst (Fig. 167).

(2) *The catalyst.* Osmium and iron were catalysts used by Haber in his early experiments (1908–1914). Iron, molybdenum, platinum, and recently, iron promoted with potassium and aluminum oxides have been used.

(3) *Temperature and Pressure.* In accordance with LeChatelier's Principle, the reaction

$$N_2 + 3H_2 \rightarrow 2NH_3 + 21{,}880 \text{ cals.},$$

should be forced to the right **at high pressure and low temperature.** (Reread sections **215–216.**) This is confirmed in the data in Table 104.

TABLE 104. PERCENTAGE OF AMMONIA AT EQUILIBRIUM

| Temperature | 1 Atmosphere | 100 Atmospheres | 1000 Atmospheres |
|---|---|---|---|
| 200° | 5 | 80 | 98 |
| 400° | 0.5 | 30 | 50 |
| 600° | 0.05 | 4.5 | 20 |

The Haber process operating at 500° and 200 atmospheres pressure gives a yield of under 8 per cent $NH_3$, so that after ammonia is removed by liquefying it, the unchanged gases are re-circulated through the catalyst (Fig. 168). The pressure is maintained by the admission of fresh gas. Only one minute elapses from the moment when the nitrogen and hydrogen enter the catalyst chamber to the time when liquid ammonia drips into the cooling chambers.

The higher the pressure, the greater the yield of ammonia. Engineering research has made it possible now to carry on the ammonia synthesis at "superpressures" up to 2000 atmospheres (modified **Claude process**) in the duPont ammonia plant at Belle, W. Va. The process is usually carried out at 900 atmospheres with five catalyst units in series and with removal of liquid ammonia between each stage. The residual gas after the fifth unit is not further used.

**c. From Soft Coal.** During the distillation of coal (**487**) an *ammoniacal liquor* is obtained. This is heated in a vessel with lime and the distillate collected in sulfuric acid:

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4.$$

This salt may be obtained by evaporation of the solution until crystallization sets in. A ton of coal ordinarily yields about 20 pounds of ammonium sulfate, worth about 30 cents. Ammonia is, therefore, one of the valuable by-products of the coke oven. In 1939 the coke ovens yielded 436,931 tons of ammonium sulfate and 20,363 tons of anhydrous ammonia.

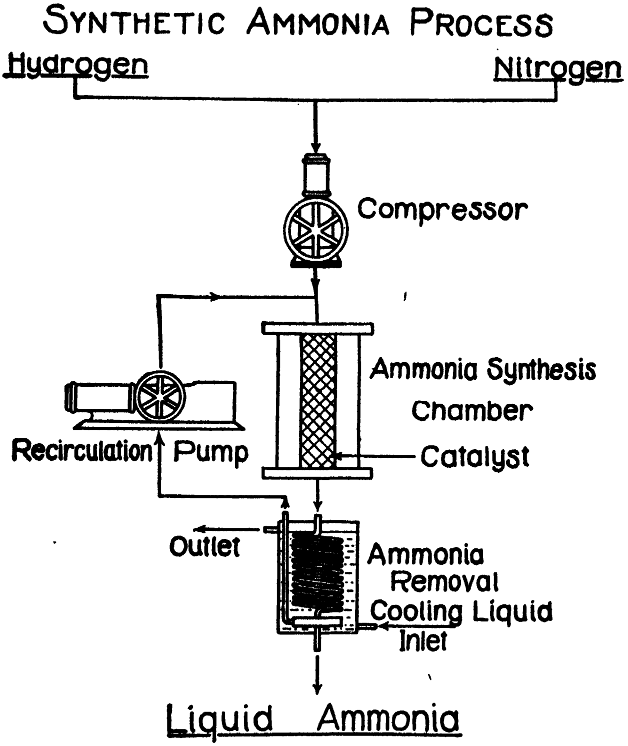


FIG. 168. Flow-sheet of the Haber process.

**d. The Cyanamide Process.** This process depends upon the decomposition of calcium cyanamide, $CaCN_2$ (504), by the action of superheated steam:

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3 \uparrow.$$

The product is very pure, and a yield of 96 to 97 per cent is claimed.

During the first World War the government cyanamide plant at Muscle Shoals had a capacity of 40,000 tons of ammonia; but this is less than 1 per cent of the total capacity by the Haber method.

**515. Physical Properties.**—Ammonia is a colorless gas with a pungent odor and a caustic taste. C.T. is 132.9° at 112.3 atmospheres pressure.

### DEMONSTRATION 131. LIQUEFACTION OF AMMONIA

Materials: Three-liter flask of ammonia gas; stopper carrying a short capillary tube and a 100 cc. pyrex tube; Dry Ice; a mixture of 50 cc. chloroform and 50 cc. carbon tetrachloride, 400 cc. beaker.

If a cold mush of Dry Ice (solid $CO_2$) with chloroform-carbon tetrachloride is lowered into the flask of ammonia, liquid ammonia collects as bluish drops. B.P. $-33.2°$, F.P. $-77°$. Some years ago a whole new world of chemistry was unfolded by the work of Frankland and Kraus in studies of reactions carried out using liquid ammonia as a solvent.

Ammonia gas is extremely soluble in water, 1300 volumes at S.T.P. dissolving in 1 volume of water. This may be demonstrated readily by means of an **ammonia fountain** similar to Dem. 51, section **144**, substituting $NH_3$ for HCl:

$$\underset{\text{ammonia gas}}{NH_3} + H_2O \rightleftarrows \underset{\text{ammonium hydroxide}}{NH_4OH} \rightleftarrows \underset{\text{ammonium ion}}{NH_4^+} + OH^-.$$

**516. Chemical Properties.**—Ammonia is not very stable, and dissociates into its elements almost completely at 700°.

### DEMONSTRATION 132. AMMONIA BURNING

Materials: Rubber tubing and 10 mm. glass tubing leading from an oxygen tank into a 1 cm. layer of concentrated ammonium hydroxide in a large test-tube; burner.

When oxygen is bubbled rapidly through very concentrated ammonium hydroxide, the issuing gas burns with a yellow flame at the mouth of the tube. CARE: *light with a burner, not a match, since the combustion is violent.*

$$4NH_3 + 3O_2 \rightarrow 6H_2O + 2N_2.$$

Under different conditions NO is formed (**529**, *b*).

### DEMONSTRATION 133. SMOKE SCREEN

Materials: Wooden box 2′ × 1′ × 3′ high. Cut a 6″ hole in the front; hinge the upper four-fifths of the back so that it may be pushed inwards, and the lower one-fifth of the back so that it may be lifted outwards. Concentrated HCl and concentrated $NH_4OH$.

Place crystallizing dishes containing HCl and $NH_4OH$ respectively in the box. Upon punching the back of the box inwards smoke rings are blown:

$$NH_3 + HCl \rightarrow \underset{\text{white clouds}}{NH_4Cl} \uparrow .$$

Ammonia, when heated, is a reducing agent, due to the hydrogen liberated. Thus, hot cupric oxide may be reduced in a tube by passing $NH_3$ over it:

$$3CuO + 2NH_3 \rightarrow 3Cu + N_2 + 3H_2O.$$

**517. Ammonium compounds.**—These have already been discussed in connection with the alkali metals (**312**), which the ammonium radical ($NH_4^+$) resembles. Most ammonium salts are unstable, and decompose upon heating (**508**, **509**, **514**).

DEMONSTRATION 134. ANALYSIS FOR $NH_4^+$

**Materials**: Mortar and pestle, litmus paper, solid NaOH and $NH_4Cl$; burner under a 1-liter distilling flask leading into a beaker of water; phenolphthalein-indicator solution.

If NaOH is added to some $NH_4Cl$ solution in the distilling flask and the mixture warmed, the $NH_3$ distills over into the beaker of water and may be tested with litmus. Even solid $NH_4Cl$ and NaOH ground together will evolve sufficient $NH_3$ to turn moistened litmus blue. **This is an analytical test for the $NH_4^+$ ion:**

$$NH_4Cl + NaOH \rightarrow NaCl + H_2O + NH_3.$$

**518. Uses of Ammonia.**—Liquid ammonia is sold in specially constructed tank cars. Its most important use, by far, is in the manufacture of nitric acid by the Ostwald Process (**529**, *b*), from which our fertilizers and explosives are made. Ammonia is likewise consumed in the Solvay Process for sodium carbonate (**303**), and as an industrial source of hydrogen (47). **Household ammonia** is made by dissolving $NH_3$ in water; and to this, ammonium carbonate is often added, giving a cloudy appearance. Ammonium chloride is used in dry cells (**198**), and in soldering.

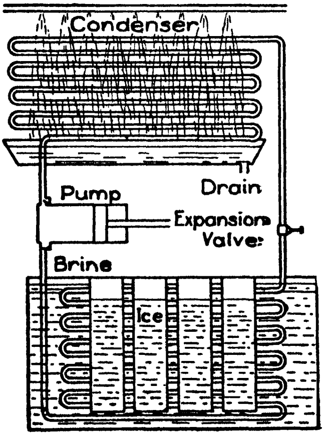


FIG. 169. The manufacture of ice by circulating liquid ammonia through pipes immersed in brine.

**Liquid ammonia** is used as a refrigerant. For this purpose the liquid ammonia is circulated through pipes immersed in brine ($CaCl_2$ is used); here the ammonia evaporates and cools the brine to about 20° below the freezing point of water. Cans of water immersed in the brine are quickly cooled and ice is formed (Fig. 169). The ammonia gas is compressed and pumped back into the condenser tubes, and the cycle is repeated.

Household electric refrigerators operate upon exactly the same principle, but use sulfur dioxide which does not have to be compressed so highly as ammonia (B.P. $SO_2$ $-10°$, B.P. $NH_3$ $-33.3°$). Lately sulfur dioxide is being replaced by an odorless and non-toxic gas, developed by Midgley of tetraethyl-lead fame. It is called "*Freon*" ($CCl_2F_2$), dichloro-difluoro-methane (B.P. $-29.8°$). However, ammonia will continue to be used in industrial ice machines and cold storage because it has so high a heat of vaporization: 1 g. of $NH_3$, in evaporating, consumes 302 calories of heat, as contrasted with 91 calories for $SO_2$, and 36 calories for $CCl_2F_2$.

### HALOGEN COMPOUNDS OF NITROGEN

**519. Halogen Compounds.**—When a solution of $NH_4Cl$ is treated with an excess of chlorine, drops of an oily liquid, **nitrogen trichloride** ($NCl_3$), may be obtained:

$$NH_4Cl + 3Cl_2 \rightarrow NCl_3 + 4HCl.$$

This compound was first prepared by Dulong (1811). It is an oily liquid of pale-yellow color, and extremely explosive. Dulong lost an eye and three fingers in preparing it, and Faraday and Davy were also injured in conducting experiments with the substance.

**Nitrogen triiodide,** $NI_3$, $NH_3$, may be prepared by treating iodine dissolved in KI solution with concentrated ammonia. The compound is obtained in the form of a brown precipitate. It may be handled while wet, but when dry it explodes with great violence, liberating iodine, as well as nitrogen. The gentle touch of a feather, or the tread of a fly, is sufficient to explode it.

## QUESTION REVIEW

I. NITROGEN.

**a. Importance (508). History and preparation (509).**

1. Draw the nitrogen cycle. In what form is nitrogen present in our bodies?
2. What rôle does copper play in the preparation of nitrogen from air?

**b. Physical properties (510). Chemical properties (511).**

3. Can nitrogen be liquefied under great pressure at room temperature? Is gaseous nitrogen heavier than air?
4. Give equations showing the combination of nitrogen with a metal. With a non-metal.

**c. The fixation of nitrogen (512).**

II. AMMONIA.

**a. History (513). Manufacture (514).**

5. What are the approximate tonnages of nitrogen fixed by different means?
6. Account for the name "spirits of hartshorn."
7. Describe in detail the preparation of hydrogen and nitrogen for use in the Haber process.
8. Discuss the application of LeChatelier's Principle in the Haber process. Why did not Haber use "super-pressures"?
9. Using the data provided in Sections 514 and 487, calculate the tons of ammonium sulfate fertilizer which might have been produced by the by-product coke industry. How much was actually produced?

**b. Physical properties (515). Chemical properties (516).**

10. In demonstration 131 might solid $NH_3$ be obtained?
11. Which is more soluble in water: $NH_3$, HCl, or $SO_2$?
12. Write equations showing the reaction of ammonia with oxygen. With HCl.
13. What chemical property of ammonia is associated with the fact that it dissociates almost completely at 700°?

**c. Ammonium compounds (517).**

14. Describe how you would analyze for $NH_4^+$.

**d. Uses of ammonia (518).**

15. Name three important industrial uses for ammonia, and copy the equations illustrating these uses.

16. Describe in detail the use of ammonia as a refrigerant. Contrast those physical properties for $NH_3$, $SO_2$ and $CCl_2F_2$ which have a bearing on this use.

III. HALOGEN COMPOUNDS OF NITROGEN (519).

**Reading References:** Articles in the Appendix:

*Ammonia:* 117 and 150.

*Nitrogen fixation:* 51, 101, 103, 114, 215, 230, 252, 304, 313, 346, 406, 408, 411 and 416.

# CHAPTER XXXVI

## OXIDES AND ACIDS OF NITROGEN

**520. The Valences of Nitrogen.**—Nitrogen exhibits valences from −3 to +5. A table of important compounds exemplifying these valences, together with salient facts concerning the substances, follows.

TABLE 105. THE VALENCES OF NITROGEN

| VALENCE | SUBSTANCE | IMPORTANT FACTS |
|---|---|---|
| −3 | $NH_3$ | Haber process; source of nitric acid for fertilizers and explosives |
| −2 | $NH_2-NH_2$ | Hydrazine |
| −1 | $NH, H_2O$ | Hydroxylamine ($NH_2-OH$) |
| 0 | $N_2$ | Nitrogen cycle |
| +1 | $N_2O$ | Nitrous oxide, laughing gas |
| +2 | $NO$ .......... | Nitric oxide |
| | from Cu plus | dilute $HNO_3$<br>concentrated $HNO_3$ |
| +4 | $NO_2$ .......... | Nitrogen dioxide<br>(red) $2NO_2 \rightleftarrows$ (colorless) $N_2O_4$ |
| +3 | $N_2O_3$ .......... | Nitrogen trioxide |
| | acid anhydride of | $HNO_2$, nitrous acid<br>$HNO_3$, nitric acid |
| +5 | $N_2O_5$ .......... | Nitrogen pentoxide |

### NITROUS OXIDE, LAUGHING GAS, $N_2O$

**521. Preparation.**—*Nitrous oxide*, or *laughing gas*, was first prepared by Priestley in 1772. The gas is prepared very readily by gently heating ammonium nitrate:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O + 9{,}000 \text{ cals.}$$

Owing to the fact that this reaction is exothermic, care must be exercised not to over-heat the ammonium nitrate. The gas may be collected over warm water or over mercury (Fig. 170).

**522. Properties.**—**Nitrous oxide** is a colorless gas having a faint, pleasant smell and a sweet taste.

Physical properties: B.P. −89.8°. C.T. 36.5°. C.P. 71.65 atmospheres. Liquefies at 0° at 30 atmospheres pressure. Solubility in 1 vol. of water: 1.3 vols. at 0°, and 0.596 vols. at 25°; more soluble in alcohol.

When nitrous oxide is inhaled by man and animals, it produces a remarkable effect. This physiological effect was first observed by Humphry Davy, who breathed 16 quarts of the gas, and afterwards wrote:

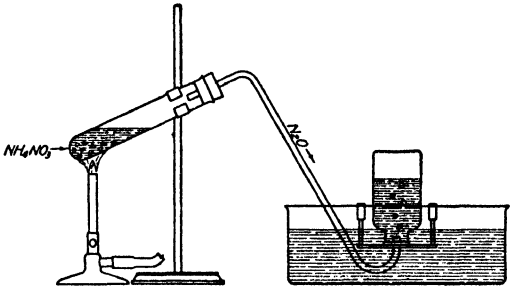


FIG. 170. The preparation of laughing gas.

> "This gas raised my pulse upward of 20 strokes, made me dance about the laboratory like a madman, and has kept my spirits in a glow ever since."

Liquid nitrous oxide, sold in small tanks, is used as an anesthetic in surgical operations, especially in dentistry. For use as such, it must contain neither nitric oxide nor chlorine; and, to prevent suffocation, it must be mixed with oxygen.

Nitrous oxide is a supporter of combustion, but not as active as is free oxygen. Thus, a glowing splinter and phosphorus will burn brilliantly in an atmosphere of the gas, forming oxides and free nitrogen. *Nitrous oxide, unlike oxygen, does not combine with nitric oxide* (NO) *to form red-brown fumes.* This test serves to distinguish the two gases.

## NITRIC OXIDE, NO

**523. Preparation.**

(*a*) Nitric oxide is usually prepared for laboratory use by the action of dilute nitric acid (sp. gr. 1.2) on copper turnings:

$$3Cu + 8HNO_{3\,dil.} \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

The gas is purified to a certain extent by passing it through water and caustic soda. It is collected over water. Nitric acid also interacts with zinc, mercury, silver, etc., to form nitric oxide.

(*b*) A one-time important method for the fixation of nitrogen (**529,** *c*) was by electric discharge through the air:

$$N_2 + O_2 + 43{,}200 \text{ cals.} \rightleftarrows 2NO.$$

**524. Properties.**—Nitric oxide is a colorless gas. **Nitric oxide is the most stable oxide of nitrogen:** even at 900°, decomposition is only slight.

Physical data: B.P. $-150°$. C.T. $-93.5°$. C.P. 71 atmospheres. Only slightly soluble in water.

Nitric oxide supports the combustion of phosphorus, but burning wood or sulfur are extinguished when introduced into the gas. NO quickly reacts with oxygen at room temperature to form red fumes of nitrogen dioxide:

$$\underset{\text{colorless}}{2NO} + O_2 \rightarrow \underset{\text{red}}{2NO_2}.$$

### NITROGEN DIOXIDE, $NO_2$. NITROGEN TETROXIDE, $N_2O_4$

**525. Preparation.**—Nitrogen dioxide, sometimes called *nitrogen peroxide,* is prepared by heating the nitrate of a heavy metal such as lead nitrate:

$$Pb(NO_3)_2 \rightarrow PbO + \tfrac{1}{2}O_2 + \begin{array}{l} 2NO_2 \text{ (nitrogen dioxide)} \\ \downarrow\!\uparrow \\ N_2O_4 \text{ (nitrogen tetroxide)} \end{array}$$

Both $NO_2$ and $N_2O_4$ are obtained, their relative amounts depending upon the temperature (526). If the gas is liquefied by passing it into a U-tube surrounded by ice-water, $N_2O_4$ collects as a pale-yellow liquid.

Nitrogen dioxide may likewise be formed by the direct action of oxygen on nitric oxide (522).

Copper, which forms NO with dilute nitric acid (**523,** *a*), forms $NO_2$ with concentrated nitric acid, the latter being such a powerful oxidizing agent that any NO which might form is oxidized up to $NO_2$:

$$Cu + 4HNO_{3\,(\text{conc.})} \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2.$$

**526. Properties.**—Nitrogen tetroxide possesses a disagreeable odor and is somewhat poisonous. It may be obtained as a pale-yellow liquid which boils at 22°. At −9.4°, it forms a mass of colorless crystals. When the liquid is allowed to evaporate, it forms a reddish-brown gas, the color of which deepens as the temperature is raised.

DEMONSTRATION 135. POLYMERIZATION OF $NO_2$

Materials: Two sealed pyrex tubes containing $NO_2$ gas; square of asbestos over burner; ice-water.

When one of the tubes is gently warmed, the following equilibrium is displaced to the left, and the gas deepens in color; when the other tube is left in ice-water, the equilibrium is displaced to the right, and the gas become pale brown:

$$\left.\begin{array}{ccc} \underset{\text{the monomer}}{2NO_2} & \underset{\text{de-polymerization}}{\overset{\text{polymerization}}{\rightleftarrows}} & \underset{\text{the polymer}}{N_2O_4.} \\ \\ \text{reddish brown} & \underset{\text{heated}}{\overset{\text{cooled}}{\rightleftarrows}} & \text{colorless} \end{array}\right\}$$

*Question:* Is the polymerization reaction exothermic or endothermic? Apply LeChatelier's Principle (**216**).

If both tubes are left at the same temperature, the colors become identical, showing that the same equilibrium mixture is formed.

The percentages at equilibrium are:

| Temperature | 22° | 60° | 156° |
|---|---|---|---|
| $NO_2$ (red) | 0% | 50% | 100% |
| $N_2O_4$ (colorless) | 100% | 50% | 0% |

The single unit, $NO_2$, is called the **monomer**; monomers combine to form the **polymer.** This typifies a class of reactions known as **polymerizations.** Such reactions are becoming increasingly important in our test-tube civilization, for many of our synthetic materials, including plastics, rubber, and artificial fibers, are made by forming giant polymer molecules containing clusters of thousands (not 2 as in the case of $N_2O_4$) of monomer units.

Above 156° nitrogen dioxide begins to decompose, the dissociation being complete above 600°:

$$\underset{\text{red}}{2NO_2} \rightarrow \underset{\text{colorless}}{2NO} + O_2.$$

The products obtained from the reaction of $NO_2$ with water depend upon the temperature:

**with cold water:** $2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$.
**with hot water:** $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$.

In the foregoing equations the gaseous reactant obviously consists chiefly of $N_2O_4$ when cold water is used, and of $NO_2$ in the case of hot water.

### NITROGEN TRIOXIDE, $N_2O_3$. NITROGEN PENTOXIDE, $N_2O_5$

**527. Acid Anhydrides.**—Nitrogen trioxide and nitrogen pentoxide may be considered as the anhydrides of nitrous and nitric acids respectively:

$$N_2O_3 + H_2O \rightarrow 2HNO_2 \text{ (nitrous acid)},$$
$$N_2O_5 + H_2O \rightarrow 2HNO_3 \text{ (nitric acid)}.$$

**Nitrogen trioxide** is quite unstable, but it may be obtained in a more or less impure form by cooling a mixture of nitric oxide and nitrogen peroxide to a low temperature, −21° or lower:

$$NO + NO_2 \rightleftarrows N_2O_3.$$

The compound condenses to a bluish liquid. It is usually assumed that nitrogen trioxide acts as a catalyst in the production of sulfuric acid by the chamber process (586), but at the temperature of the operation only NO and $NO_2$ could exist.

**Nitrogen Pentoxide** can be obtained by treating anhydrous nitric acid (hydrogen nitrate) with phosphorus pentoxide, which abstracts from it the elements of water:

$$2HNO_3 + P_2O_5 \rightarrow N_2O_5 + 2HPO_3.$$

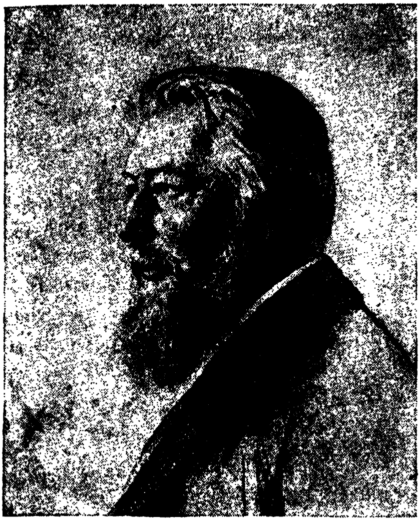
It may be obtained as a white crystalline solid, which decomposes between 45° and 50°. It is of no practical importance.

### NITRIC ACID, $HNO_3$

**528. History.**—Nitric acid (*aqua fortis*) was prepared by the alchemists, who used it as a reagent for separating silver from gold. Glauber was probably the first to prepare the acid from potassium nitrate and sulfuric acid—a method of preparation still in use. Cavendish (1785) established the composition of nitric acid synthetically. He passed a discharge of electricity through oxygen and nitrogen in the presence of water or alkaline solutions, which absorbed the oxides of nitrogen.

**529. Preparation and Manufacture.**—

**a. From Natural Nitrates.**—The principal source of natural nitrates is a large deposit of sodium nitrate, $NaNO_3$, found in the rainless districts of Chile and Peru. **Chile saltpeter,** as it is



WILHELM OSTWALD
(1853–1939)

Director of the Physico-Chemische Institut at Leipzig from 1887 until his retirement in 1906; a pioneer of modern physical chemistry when, with Van't Hoff, he championed the Arrhenius theory of ionization. In 1887 they published the Zeitschrift für Physikalische Chemie. Ostwald was awarded the Nobel Prize in 1909, chiefly for his work on the electrochemistry of solutions. In 1900 he developed the method for oxidizing ammonia to nitric acid, which stimulated the researches by Fritz Haber.

FRITZ HABER (1868–1934)

His important researches on the synthesis of ammonia (1908–1914) laid the foundation for the enormous industry of fixing nitrogen from the air for fertilizers and explosives; in recognition of this work he shared a Nobel Prize with Carl Bosch, who developed the industrial aspects of the process. Haber was director of the Kaiser Wilhelm Institut für Physikalische Chemie at Berlin-Dahlem until 1933. He is distinguished for his pure research in the fields of catalysis, electrochemistry and thermochemistry.

commonly called, occurs in a deposit 220 miles long, 2 miles wide, and about 5 feet thick; it contains from 20–75 per cent of $NaNO_3$. The fact that the sodium nitrate is mixed with sodium chloride and other salts probably indicates that the region was at one time covered by the sea.

Another source of nitric acid is **potassium nitrate**, $KNO_3$, commonly known as saltpeter or niter. This compound is found especially in the neighborhood of Oriental cities from the decomposition of urea in urine in contact with potash contained in the soil.

**Both an industrial and the laboratory method** for preparing $HNO_3$ depend upon the interaction of these natural nitrates with sulfuric acid. The results in the two instances differ because the industrial method uses a higher temperature:

$$\text{Laboratory:}\quad NaNO_3 + H_2SO_4 \xrightarrow{\text{warm}} NaHSO_4 + HNO_3,$$

$$\text{Industrial:}\quad 2NaNO_3 + H_2SO_4 \xrightarrow{\text{hot}} Na_2SO_4 + 2HNO_3.$$

*Question:* From the foregoing facts, deduce whether $H_2SO_4$ or $NaNO_3$ must be the more expensive reactant.

In either case the $HNO_3$ volatilizes off (B.P. 86°) and may be readily condensed. In industry, the reaction is carried out in iron retorts, and the nitric acid vapors are condensed in receivers cooled by running water. Owing to the fact that the higher temperature partly decomposes the nitric acid, the process is not an economical one. The distillate obtained, even at the lower temperature, has a yellowish color, caused by the presence of $NO_2$; for when $HNO_3$ is heated, it is partially decomposed into water, oxygen, and nitrogen peroxide. Pure hydrogen nitrate may be obtained by heating $NaNO_3$ and $H_2SO_4$ in a retort under diminished pressure and by cooling the vapor.

Sodium bisulfate, or "niter cake," which is a by-product of the manufacture of nitric acid, is used extensively in the bleaching, dyeing, and textile industries; in pickling and cleaning metals; and in the manufacture of hydrochloric acid (143).

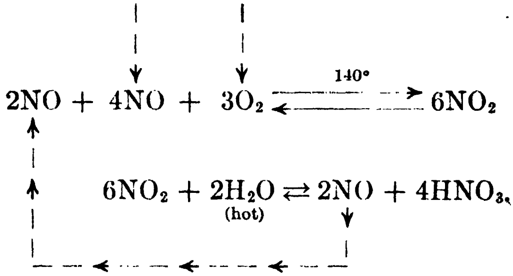
**b. From Ammonia (Ostwald Process).**—This is the chief industrial method for preparing nitric acid. Developed by the great German physical chemist Wilhelm Ostwald in 1900, it enabled Germany to produce great quantities of explosives after the supply of Chile saltpeter was cut off by British blockade during the World War of 1914–1918. By 1939 all belligerents were manufacturing their nitric acid, which is an intermediate in the manufacture of explosives, by this method.

A mixture of 10 volumes of air and 1 volume of ammonia, at 1 to 8 atmospheres of pressure, is passed through a nickel tube containing layers of incandescent platinum gauze or base-metal oxides. Catalyst temperatures in the range 830–900° give conversion efficiencies as high as 99 per cent:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O + 214{,}200 \text{ cals.}$$

Since the oxidation is exothermic, artificial heating is not required except at the beginning.

When the reaction mixture cools, the excess oxygen oxidizes NO to $NO_2$. This is absorbed in warm water, forming $HNO_3$ and NO. The NO is recirculated as indicated below.



### DEMONSTRATION 136. THE OSTWALD PROCESS

Materials: Burner; concentrated $NH_4OH$; 1 cm. length of platinum coil suspended in the middle of a 6″ square of asbestos board; hole cut in asbestos to pass a glass tube from an oxygen tank; 5 cm. crystallizing dish; burner.

Concentrated $NH_4OH$ is poured into the dish so that the Pt-coil will come within a few mm. of its surface. Oxygen is run in gently. The Pt-coil is momentarily heated, then quickly lowered into the $NH_3$ vapors so that the oxygen plays upon its surface. The above reactions take place, reddish-brown $NO_2$ being observed.

**c. From the air (Arc Process).**—A process formerly employed, but now obsolete, is to form NO by passing an electric arc through air. Even at 3000° only 5 per cent NO is formed. The subsequent treatment of the NO to form $HNO_3$ is the same as in the Ostwald process. This process was once used extensively in Norway (Birkland-Eyde Process).

**530. Physical Properties.—Nitric acid, $HNO_3$,** is a colorless liquid which boils at 86° and has a sp. gr. of 1.52. The liquid may be frozen to a snow-like solid which melts at −47°. When very concentrated nitric acid is distilled, a portion of the compound decomposes; the acid becomes constantly weaker until it contains 68 per cent $HNO_3$. At this point the liquid boils unaltered at 120.5°, yielding a distillate having a sp. gr. of 1.414 at 15.5°. If, on the other hand, acid less concentrated than this is distilled, the concentration of the residue increases until it contains 68 per cent $HNO_3$. This "*constant boiling mixture*" (See HCl, 144) containing 68 per cent $HNO_3$ is the concentrated nitric acid of commerce. **"Fuming nitric acid"** is the concentrated acid containing nitrogen dioxide in solution.

**531. Chemical Properties.**—

**a. Nitric acid is unstable.** When heated, or in sunlight, $NO_2$ is formed:

$$4HNO_3 \rightarrow 2H_2O + 4NO_2 \uparrow + O_2 \uparrow .$$

**b. Nitric acid is corrosive.** It attacks the skin, producing painful wounds, and is employed in surgery as a cautery. The diluted acid colors skin, nails, wool, silk, etc., yellow.

**c. Nitric acid is a powerful oxidizing agent.**

### DEMONSTRATION 137. OXIDIZING ACTION OF $HNO_3$

Materials: (*a*) 100 cc. beaker containing 5 cc. conc. $H_2SO_4$ and 25 cc. fuming nitric acid placed inside a 2 liter beaker, table protected with 1′ square of asbestos board; test-tube, containing 2 cc. turpentine, taped to end of meter-stick, (*b*) penny, 200 cc. beaker, concentrated nitric acid.

CARE: (*a*) When the turpentine is poured into the acid mixture, it is quickly oxidized, igniting violently. (*b*) A penny treated with nitric acid gives off reddish-brown clouds of $N_2O_4$.

When **the metals** in the electromotive series preceding hydrogen are treated with dilute nitric acid, hydrogen is displaced as it is from other acids. If the **metal** is **more active than zinc** (*e.g.*, Mg) a considerable part of the hydrogen escapes oxidation. In the case of **zinc and less active metals**, most or all of the hydrogen is oxidized to water. With zinc, a portion of the $N^{+5}$ is reduced to $N^{-3}$, as ammonia; this interacts with more acid to form ammonium nitrate. With copper, the $N^{+5}$ is reduced to $N^{+4}$ or $N^{+2}$. Platinum, gold, and a few rare metals are not oxidized by nitric acid.

**Non-metals,** too, are attacked. Carbon is oxidized to carbon dioxide, sulfur to sulfuric acid, and phosphorus to phosphoric acid.

Equations representing the foregoing reactions are given below. The student should employ either the electron method (**134**) or the step-wise method (**417**) for balancing these difficult equations.

$$
\begin{aligned}
Mg + 2HNO_{3\,\text{dil.}} &\rightarrow Mg(NO_3)_2 + H_2 \uparrow, \\
4Zn + 10HNO_{3\,\text{dil.}} &\rightarrow 4Zn(NO_3)_2 + 3H_2O + NH_4NO_3, \\
3Cu + 8HNO_{3\,\text{dil.}} &\rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO \uparrow, \\
Cu + 4HNO_{3\,\text{conc.}} &\rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2 \uparrow, \\
3P + 2H_2O + 5HNO_{3\,\text{dil.}} &\rightarrow 3H_3PO_4 + 5NO \uparrow.
\end{aligned}
$$

From equations 3 and 4 it is evident that the more concentrated the acid, the less the valence change of the $N^{+5}$. This is a general rule.

**d. Aqua Regia.** This reagent is prepared by mixing 1 vol. of concentrated nitric acid and 3 vols. of hydrochloric acid. They interact to form chlorine and nitrosyl chloride (NOCl):

$$HNO_3 + 3HCl \rightarrow 2H_2O + Cl_2 + NOCl.$$

It is a powerful oxidizing agent and solvent. Thus, it readily dissolves gold and platinum. This reagent was well known to the alchemists, who called it *aqua regia* on account of its great solvent action.

**e. Nitric acid for explosives.** About 75 per cent of the output of nitric acid is used in the manufacture of explosives (**534**) and nitrate fertilizers. Explosives are just as important peace-time tools for mining, construction work, clearing farm land, etc., as they are vital weapons of death during war-time.

**532. Nitrates.**—The salts of nitric acid, or nitrates, are among the most important compounds known. Thus, *sodium nitrate* and *potassium nitrate* are valuable fertilizers and the chief source of nitric acid. *Ammonium nitrate*, $NH_4NO_3$, is an important explosive. *Barium nitrate*, $Ba(NO_3)_2$, and *strontium nitrate*, $Sr(NO_3)_2$, are used in pyrotechny; and *silver nitrate*, $AgNO_3$, is used in photography, the manufacture of indelible ink, as a cautery in medicine, etc.

In general, the nitrates are soluble in water and are decomposed by heat.

A nitrate (or nitric acid) may be recognized by the following test:

Dissolve a small quantity of nitrate in water, add an equal volume of concentrated sulfuric acid, and then cool the mixture to room temperature. Incline the test-tube containing the liquid, and carefully pour down its side a concentrated solution of freshly prepared ferrous sulfate, $FeSO_4$, so that the liquids mix only at the surface of contact. A dark-brown ring appearing at the junction of the liquids indicates the presence of a nitrate. The sulfuric acid interacts with $NaNO_3$ to liberate $HNO_3$ which is reduced by $FeSO_4$ to nitric oxide (NO). The excess of $FeSO_4$ will then absorb NO to give a brown color—a delicate test for nitric acid or a nitrate.

## NITROUS ACID AND NITRITES

**533. Nitrous Acid and Nitrites.**—As stated above (527) nitrogen trioxide is the anhydride of nitrous acid, $HNO_2$.

The acid is known only as a water solution, which is pale blue. This solution of $HNO_2$ may be obtained by acidulating an aqueous solution of one of its salts:

$$\underset{\text{sodium nitrite}}{NaNO_2} + H_2SO_4 \rightarrow NaHSO_4 + \underset{\text{nitrous acid}}{HNO_2}$$

The $HNO_2$ is unstable, and evolves NO upon warming; this NO combines with the oxygen of the air to form reddish brown $NO_2$:

$$\begin{array}{l} 3HNO_2 \rightarrow 2NO + HNO_3 + H_2O \\ \phantom{3HNO_2 \rightarrow}\ \downarrow \\ \phantom{3HNO_2 \rightarrow} 2NO + \text{air} \rightarrow 2NO_2 \text{ (reddish brown).} \end{array}$$

These reactions serve in analysis to differentiate between a nitr*ate* and a nitr*ite*: the latter evolves a brown gas ($NO_2$) upon treatment with acid.

**Nitrites**, the salts of nitrous acid, are stable compounds. They may be prepared (*a*) by fusing sodium nitrate either alone or with lead; or (*b*) by treating an alkali with nitrogen trioxide (rather with a mixture of nitrogen dioxide and nitric oxide):

(*a*) $$2NaNO_3 \rightarrow 2NaNO_2 + O_2 \uparrow,$$

(*b*) $$2NaOH + NO_2 + NO \rightarrow 2NaNO_2 + H_2O.$$

## NITROGEN COMPOUNDS IN PEACE AND WAR

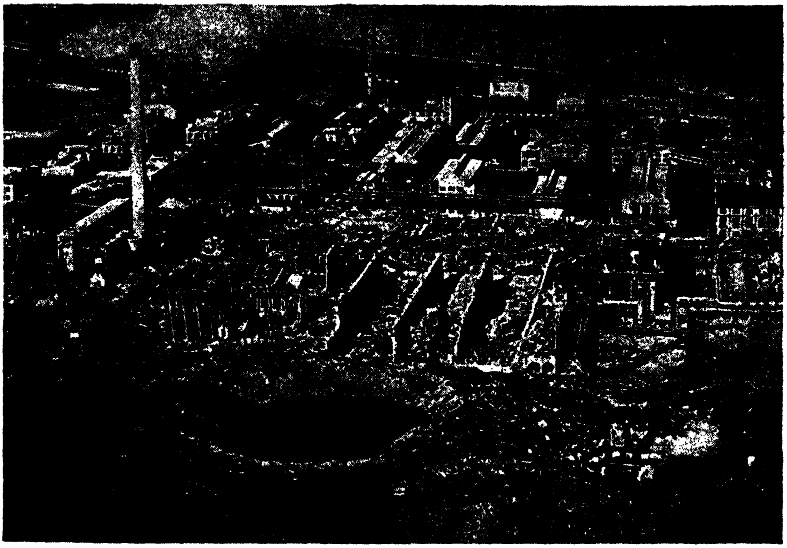
**534. Nitrate Explosives.**—We have seen that nitric acid is a powerful oxidizing agent. Nitrates, too, possess this property, and will vigorously oxidize substances with which they are mixed.

### DEMONSTRATION 138. EXPLOSIVE NATURE OF NITRATES

Materials: (*a*) Solid $KNO_3$ in evaporating dish over burner, horn spoon, powdered charcoal; (*b*) paper written on with $KNO_3$ solution, cord dipped in saturated $KNO_3$ solution and dried; (*c*) (CARE: *do not grind; do not mix in a mortar*) 30 g. powdered $KNO_3$, 5 g. charcoal, 5 g. sulfur gently mixed on a sheet of asbestos, smokeless powder cartridge; (*d*) 30 g. of zinc dust placed upon a pile of 30 g. of very dry $NH_4NO_3$ on an asbestos board, pipette.

(*a*) Charcoal sifted into molten $KNO_3$ flares up and is oxidized. (*b*) Upon lighting the cord or the writing on paper, the $KNO_3$ burns steadily: this is a fuse. (*c*) $KNO_3$, S and C are the ingredients of old-fashioned gunpowder. They will burn fiercely, but not explosively. If a little pile of ordinary smokeless powder from a cartridge is lighted in the same way, it will flash almost explosively, demonstrating that the fineness of division and compression of the powder makes it much more dangerous. (*d*) A drop of water upon the dry powder gives volumes of smoke clouds.

FIG. 171 shows an industrial explosion which occurred in 1920 when thousands of tons of ammonium nitrate exploded at the Badische Aniline Works at Oppau, Germany. Four hundred thirty lives were lost and property damage was about $50,000,000. A hole 250 feet in diameter and over 50 feet deep was formed. During the present War (1941) a mixture of ammonium nitrate and sawdust is frequently used as an explosive.



*Courtesy of Underwood & Underwood*

FIG. 171. Results of the explosion at Oppau, Germany.

**High explosive shells** have an amazing property. They must not explode under the terrific jolt which speeds them on their way; yet, upon reaching their destination, they must be easily detonated. The secret for making these high explosives was not discovered until the middle of the 19th century.

In 1864 Alfred Nobel found that nitroglycerine, by itself a dangerously explosive liquid, could be absorbed in diatomaceous earth (German, *kieselguhr*, section 470) to form relatively inert **dynamite.** The dynamite is exploded by shock, producing enormous volumes of gases. Today dynamite is made by absorbing nitroglycerine in ammonium nitrate or in wood pulp. Although dynamite is too sensitive and violent for use in shells, it is employed on a larger scale for blasting.

**Nitroglycerine** is a misnomer, since the molecule contains *nitrate* ($NO_3$) not *nitro* ($NO_2$) groups. Its correct name is glyceryl trinitrate. It is formed by treating glycerine with a mixture of concentrated nitric and sulfuric acids. The latter removes the water formed in the reaction:

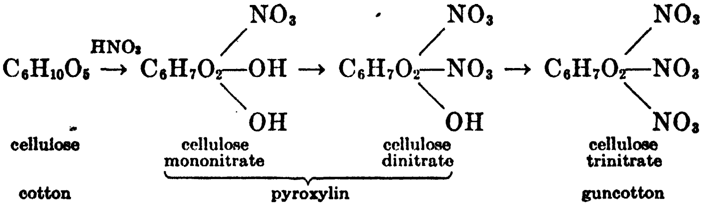
$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + 3HNO_3 \rightarrow \underset{\text{glyceryl trinitrate}}{C_3H_5(NO_3)_3} + 3H_2O.$$

The compound was discovered by the Italian chemist Sobrero in 1846, and in 1864 Nobel began its manufacture on a large scale. Liquid nitroglycerine is used for torpedoing oil and gas wells.

**Nitrocellulose,** or **guncotton,** is another explosive nitrate which is mis-named, since it, too, contains the nitrate group.

**Smokeless powders** are of two types. One, the *nitrocellulose powders*, contain nitrocellulose only. The other, *nitroglycerine powders*, consist of a mixture of nitroglycerine and nitrocellulose. *Cordite* belongs to the latter class. When smokeless powders burn, colorless gases (CO, $CO_2$, $N_2$ and $H_2O$) are formed; hence they are invisible. *Blasting gelatin* contains 9 parts of nitroglycerine and 1 part of cellulose trinitrate.

**535. Nitrated Cellulose.**—When cellulose fibers (cotton linters, the short fibers unsuitable for fabrics) are treated with a mixture of sulfuric and nitric acids, OH groups are replaced by $NO_3$ groups, *i.e.*,



$$C_6H_{10}O_5 \xrightarrow{HNO_3} C_6H_7O_2\begin{array}{l}\diagup NO_3\\ -OH\\ \diagdown OH\end{array} \rightarrow C_6H_7O_2\begin{array}{l}\diagup NO_3\\ -NO_3\\ \diagdown OH\end{array} \rightarrow C_6H_7O_2\begin{array}{l}\diagup NO_3\\ -NO_3\\ \diagdown NO_3\end{array}$$

**a. Pyroxylin.**—When cellulose is not completely nitrated, **pyroxylin** is obtained. This is made into a variety of peace-time products.

*Collodion* is a solution of pyroxylin in alcohol and ether.

*Nitrocellulose lacquers* are manufactured by heating the pyroxylin with mildly alkaline agents; this so lessens its viscosity that a solution of it in organic solvents can be sprayed as a lacquer. Pigments of the desired color are also added. Duco lacquer is an example. This new kind of paint, which has made its appearance during the past decade, differs radically from the paint which had been in use for the past four thousand years. The *drying of lacquers* involves the evaporation of the solvent, leaving a thin film of the nitrocellulose upon the object to be lacquered. The *drying of oil-paints*, on the other hand, involves oxidation and polymerization of the oil vehicle. The latter process is obviously a slow one since it entails a diffusion of oxygen through the paint layer. By development of the nitrocellulose lacquers the painting of automobiles has been reduced from a month to a matter of a few minutes.

*Nitrocellulose cements*, such as Duco cement, are similar to lacquers, but are of thicker consistency.

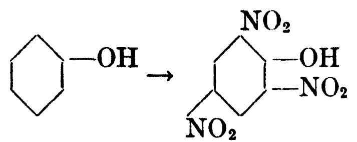
Pyroxylin is also used extensively in the manufacture of *artificial leather*, such as Fabrikoid, which is a cloth coated with the cellulose nitrate.

*Celluloid*, one of the first plastics, is produced on a large scale by working a mixture of pyroxylin, camphor and alcohol.

**b. Guncotton.** The fully nitrated cellulose, *i.e.*, cellulose trinitrate, is **guncotton**. It is exploded by a detonating cap, and when unconfined burns rapidly. One nitrating mixture used for making guncotton contains 60 per cent concentrated $H_2SO_4$, 20 per cent concentrated $HNO_3$, and the remainder water. As in making nitroglycerine, the function of the $H_2SO_4$ is to remove water formed during the course of the reaction.

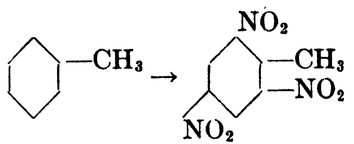
Guncotton is used in torpedoes and mines and as the basis of certain smokeless powders. It was discovered by Schönbein in 1845. In 1865, Abel improved the process of manufacture, and at the present time it is considered one of the safest of explosives, provided that it is properly manufactured. Even the mono- and di-nitrates are explosive if improperly manufactured; and chemical plants engaged in this business are equipped with special safety-chutes into which the workers can jump, sliding outside of the building to safety if the batch suspiciously smokes.

**536. Nitro-Compounds.**—A number of explosives contain the nitro ($-NO_2$) group. The two examples we shall discuss are **picric acid** and **T.N.T.** Both molecules contain a ring of six carbons, known as a "benzene ring." The arrangement of the atoms in space is sketched below.



phenol
$C_6H_5OH$

tri-nitro-phenol
AN EXPLOSIVE
(picric acid)
$C_6H_2(OH)(NO_2)_3$



toluene
$C_6H_5CH_3$

tri-nitro-toluene
AN EXPLOSIVE
(T.N.T.)
$C_6H_2(CH_3)(NO_2)_3$

**a. Picric acid.**—Picric acid, trinitrophenol, $C_6H_2(OH)(NO_2)_3$, has been known ever since the seventeenth century, when J. A. Glauber prepared it by treating wood with nitric acid. Its deep yellow crystals have long been used as a dye. Properly handled, it is quite safe: for instance, it is melted and poured into shells. It became a high explosive of utmost importance when Sprengel discovered, in 1871, that it may be detonated by fulminate of mercury; *i.e.*, that explosion of small quantity of the latter will explode a considerable mass of picric acid. Phenol, from which it is made, is also the raw material for plastics (629); and the Raschig Process for phenol which swung into operation in the United States in 1940 assures a plentiful supply.

**b. T.N.T.—Tri-nitro-toluene,** $C_6H_2(CH_3)(NO_2)_3$, is a solid, melting at 81.5°. Like picric acid, it will stand rough handling without exploding; but will explode instantly upon detonation. It is estimated that Germany, in 1940, was producing 1,500,000 metric tons of high explosives, probably consisting of mixtures of ammonium nitrate and T.N.T. During war-time toluene is normally at a premium; but by a process (625) which went into production in 1940 for the first time, unlimited quantities of toluene are now available from petroleum in the United States. The plant, at Houston, Texas, has an annual capacity of 10,000,000 gallons of toluene.

## QUESTION REVIEW

### The valences of nitrogen (520).

1. Tabulate one compound and an important fact for each of the valences of nitrogen.

### I. NITROUS OXIDE, $N_2O$, LAUGHING GAS (521–522).

2. What weight of ammonium nitrate is required to prepare 50 liters of laughing gas?
3. Can laughing gas be liquefied at room temperature by the use of pressure?

### II. NITRIC OXIDE, NO (523–524).

4. Account for the fact that when dilute nitric acid is poured upon a copper coin in the air, brown fumes are evolved.

### III. NITROGEN DIOXIDE, $N_2O$ (525–526).

5. Contrast the action of *dilute* and of *concentrated* nitric acid on copper. Of hot and of cold water on $NO_2$. Give equations.
6. Define polymerization. Why is it important? Is the polymerization of $NO_2$ an exothermic or an endothermic reaction?

### IV. NITROGEN TRIOXIDE, $N_2O_3$. NITROGEN PENTOXIDE, $N_2O_5$ (527).

### V. NITRIC ACID, $HNO_3$ AND NITRATES.

#### a. History (528). Preparation and manufacture (529).

7. Why does industry use a high temperature for obtaining nitric acid from Chile saltpeter?
8. Give equations for the Ostwald process. Why was Germany indebted to Ostwald? To Haber?

#### b. Physical properties (530). Chemical properties (531).

9. Explain what is meant by a *constant boiling mixture.* What occurs when dilute nitric acid is boiled?
10. Contrast the action of Cu, Mg, Zn and P on dilute nitric acid. Give equations.
11. State two experiments which demonstrate the oxidizing properties of nitric acid.
12. Give an equation for the action of *aqua regia* on gold.

#### c. Nitrates (532).

13. Describe the ring test for $NO_3^-$.

VI. NITROUS ACID AND NITRITES (533).

14. How would you distinguish a nitr*ite* from a nitr*ate*? Give equations.

VII. NITROGEN COMPOUNDS IN PEACE AND WAR.

**a. Nitrate explosives** (534).

15. Describe three experiments which show the explosive nature of nitrates.
16. State some important fact concerning each of the following substances: nitroglycerine, guncotton, cordite, two sorts of smokeless powders, dynamite, blasting gelatin.

**b. Nitrated cellulose** (535).

17. Show by formulas what is meant by a fully nitrated and by a partially nitrated cellulose. To what uses is each put?
18. Show by means of an equation the function of concentrated sulfuric acid in a nitrating mixture.

**c. Nitro-compounds** (536).

19. Sketch the arrangement of atoms in T.N.T. and in picric acid, showing their relation to phenol and toluene. Mention one interesting fact about each of these explosives.

**Reading References:** Articles in the Appendix:

*Explosives:* 125, 128, 311, 312, 318, 341 and 346.

*General:* 129 and 301.

*Nitrogen fixation:* 51, 101, 103, 114, 215, 230, 252, 304, 313, 346, 406, 408, 411 and 416.

# CHAPTER XXXVII

## THE NITROGEN FAMILY. GROUP V-B

**537. The Nitrogen Family.**—**Phosphorus** is below **nitrogen** in the V–B group of the Periodic Table. The other members are **arsenic, antimony and bismuth.**

TABLE 106. THE NITROGEN FAMILY

| | NITROGEN N | PHOSPHORUS P | ARSENIC As | ANTIMONY Sb | BISMUTH Bi |
|---|---|---|---|---|---|
| Atomic weight | 14.008 | 30.978 | 74.91 | 121.76 | 209.0 |
| Atomic number | 7 | 15 | 33 | 51 | 83 |
| Electron arrang. | 2–5 | 2–8–5 | 2–8–18–5 | 2–8–18–18–5 | 2–8–18–32–18–5 |
| Melting point | −209.9° | 44° | 850° | 630° | 271° |
| Sp. gr. (solid) | 1.0265 | 1.83 | 5.73 | 6.7 | 9.8 |
| Hydrides | $NH_3$ | $PH_3$ | $AsH_3$ | $SbH_3$ | ...... |
| Chlorides | $NCl_3$ | $PCl_3$ | $AsCl_3$ | $SbCl_3$ | $BiCl_3$ |
| | ...... | $PCl_5$ | $AsCl_5$ | $SbCl_5$ | ...... |
| Oxides (some) | $N_2O_3$ | $P_2O_3$ | $As_2O_3$ | $Sb_2O_3$ | $Bi_2O_3$ |
| | $N_2O_5$ | $P_2O_5$ | $As_2O_5$ | $Sb_2O_5$ | $Bi_2O_5$ |
| Acids | $HNO_3$ | $HPO_3$ | $HAsO_3$ | $HSbO_3$ | ...... |
| | ...... | $H_3PO_3$ | $H_3AsO_3$ | $H_3SbO_3$ | ...... |
| | ...... | $H_3PO_4$ | $H_3AsO_4$ | $H_3SbO_4$ | ...... |
| | ...... | $H_4P_2O_7$ | $H_4As_2O_7$ | $H_4Sb_2O_7$ | ...... |

It will be observed from the table that the members of the V–B group have valences of +3 and +5 in common. Nitrogen and phosphorus are two of the most important elements in plants and animals; they are much more abundant and widely distributed than the other three members of the family. Both nitrogen and phosphorus are acidic, and form many compounds which are analogous. On the other hand, nitrogen is a diatomic gas, while phosphorus is a solid which boils at 287° to form $P_4$; nitrogen is rather inert under ordinary conditions, whereas phosphorus is exceedingly active; nitrogen is colorless, but phosphorus is red or white.

In passing from nitrogen to bismuth, the metallic character of the element becomes more pronounced. Thus the acids of nitrogen are powerful, much more so than those formed by carbon and silicon of Group IV-B; acids of phosphorus are not so strong, but none-the-less distinctly acidic; while arsenious acid, $H_3AsO_3$, is amphoteric in character, *i.e.*, both acidic and basic. In the same sense, the oxides of nitrogen and phosphorus are acidic, while those of bismuth are basic. Also, arsenic, antimony and bismuth have a sort of metallic appearance. Moreover, bismuth does not form hydrides corresponding to $NH_3$ and $PH_3$, *i.e.*, it has no negative valence.

Nitrogen and phosphorus are strictly non-metals; but arsenic, antimony and bismuth possess certain well-defined metallic properties, so that they are classed with the metals in routine qualitative analysis.

From the foregoing discussion, it is apparent that the members of this family "run the gantlet" from non-metallic properties (N) to metallic properties (Bi).

## PHOSPHORUS $^{30.98}_{15}P$

**538. History and Occurrence.**—It is generally supposed that phosphorus was accidentally discovered by Brand, a Hamburg alchemist and merchant, in 1669. He was searching for the philosopher's stone, hoping to be able to transmute silver into gold. Brand heated white sand and the residue from evaporated urine and observed that a vapor was formed which condensed to a white, translucent solid having the marvelous properties of glowing in the dark and igniting spontaneously in the air (phosphorus, Greek, ***light* + *to bear***). Moreover, it left a luminous trail when drawn along a wall or board. The discovery of such a remarkable substance attracted a great deal of attention, and Krafft made a tour of Europe, exhibiting the glowing substance before crowned heads, including Charles II of England.

The price of phosphorus remained extremely high until 1771, when Scheele, the great Swedish chemist, discovered a method for producing it from calcium phosphate, or bone-ash, which proved to be a commercial success and was employed for over a century.

Phosphorus is widely disseminated in the combined state, making up 0.12 per cent of the earth's crust. The skeleton of man contains about 1400 g. of phosphorus, the muscles 130 g., and the brain and nerves 12 g. The element is also an essential constituent of vegetable matter, and is therefore an essential fertilizer.

The chief sources of phosphorus and superphosphate fertilizers are **phosphorite**, $Ca_3(PO_4)_2$ and **apatite**, $3Ca_3(PO_4)_2$, $CaF_2$, which occur in South Carolina, the Gulf States, and North Africa. These deposits are of fossil origin. See section 548.

**539. Preparation.**—The **electric furnace process** has been in use since 1920. An intimate mixture of phosphate, silica, and carbon is heated to a high temperature in an electric furnace (Fig. 172). The phosphorus is set free at this high temperature:

$$\underset{6CaO,2P_2O_5}{2Ca_3(PO_4)_2} + 6SiO_2 + 10C \rightarrow 10CO + \underset{\substack{\text{Calcium}\\\text{metasilicate}\\\text{(slag)}}}{6CaSiO_3} + P_4\uparrow.$$

The Monsanto Chemical Company commenced large-scale production of phosphorus in the Tennessee Valley in 1936. According to their process, the ore is first heated with coke in a sintering furnace nearly as huge as the pig-iron blast furnace. From here it passes into the electric furnace. Phosphorus volatilizes from the furnace, and the vapors are condensed; the molten phosphorus is run into four 1,000,000 lb. storage tanks. From here it is pumped into tank-cars for shipment. The slag from the electric furnace contains ferrophosphorus, which is cast into pigs for the steel industry.

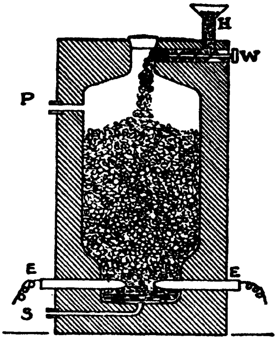


FIG. 172. Electric furnace for the production of phosphorus.

**540. Properties of Phosphorus.**—Phosphorus, like carbon, occurs in different forms, the two common varieties being **white (yellow) phosphorus** and **red phosphorus.**

Both varieties form $P_4$ vapor; between 1500° and 1700° the density of the vapor decreases, showing that dissociation occurs:

$$\text{(below 1500°)}\ P_4 \rightleftarrows 2P_2\ \text{(above 1700°)}$$

### DEMONSTRATION 139. EXPERIMENTS WITH PHOSPHORUS

Materials: (CARE: *white phosphorus is extremely dangerous; never allow solutions to touch the skin.*) (*a*) White P, forceps, rubber and glass tubing leading to bottom of pyrex tube clamped over burner; (*b*) saturated solution of white P in $CS_2$, 2″ × ½″ paper clipped to end of drinking straw, test-tube of oxygen; (*c*) oxygen tank leading to a flask of water over burner, white P, forceps.

(*a*) The transformation from white to red phosphorus may be shown by dropping some into a tube, warming until it catches fire,

TABLE 107. ALLOTROPIC FORMS OF PHOSPHORUS

| WHITE PHOSPHORUS | RED PHOSPHORUS |
|---|---|
| Very reactive; phosphoresces upon exposure to air, but does not oxidize in pure $O_2$ below 27°; extremely inflammable. | Less active; does not catch fire in air below 240°; properties vary, showing it is not a pure substance. |
| M. P. 44°; B. P. 287°; Sp. Gr. 1.83 | Does not melt on heating. Sp. Gr. 2.25. |
| Soluble in $CS_2$, ether, turpentine, etc.; insoluble in water. | Insoluble in $CS_2$, water, etc. |
| Soft; may be cut with a knife. | Red powder. |
| Crystallizes as octahedrons. | Tabular crystals. |
| Very poisonous, 0.15 g. fatal; produces a necrosis of the jawbones, "phossy jaw." | Non-poisonous; used in safety matches. |

and then quickly blowing. (*b*) Paper dipped into white P dissolved in $CS_2$ catches fire in a few seconds in the air, but not at all in oxygen. (*c*) Phosphorus melts in hot water, and burns vigorously (CARE) when oxygen is bubbled in.

Other modifications of phosphorus have been prepared and described. Thus, Bridgeman subjected white phosphorus at 200° to a pressure of 12,000 kilograms per sq. cm., and obtained a black modification having a sp. gr. of 2.691 and chemical properties similar to the red. Again, when phosphorus is crystallized from molten lead, a black form is obtained, having the appearance of a metal.

**541. Matches.**—The greatest use for elemental phosphorus is in the manufacture of **matches.** The head of a match contains an oxidizing agent and a combustible material. When rubbed on a rough surface, heat is generated by friction, and the combustible material is raised to its kindling temperature.

The manufacture of matches is an interesting process. Blocks of white pine are fed into a machine and cut into sticks, which are forced into holes of metal plates. The plates are then fastened together in the form of an endless chain, followed by treatment with appropriate materials for completing the matches. The manufacture of matches, from wood to finished products, is all done by machinery.

**Friction matches** were invented by John Walker in 1827. The old phosphorus match contained $KClO_3$ and P; but the workmen were poisoned by the phosphorus, and $P_4S_3$ was substituted for it.

### DEMONSTRATION 140. EARLY MATCHES

Materials: (*a*) Pile of finely-powdered $KClO_3$ the size of a match-head, *no more* (CARE: *grind $KClO_3$ gently; it will explode if organic matter is present*); medicine dropper; saturated solution of white P in $CS_2$ (CARE: *do not spill on hands or clothes*); (*b*) mix gently a pin-head of red P with an equal quantity of $KClO_3$; hammer.

(*a*) A minute after a few drops of the phosphorus solution is added to the $KClO_3$ there will be a violent report (CARE). This is the principle of the early match, *i.e.*, phosphorus mixed with an oxidizing agent. (*b*) Striking the mixture of red P and $KClO_3$ results in a thunderous report.

**"Safety" (Swedish) matches** were invented by Böttger in 1848. Neither phosphorus nor a compound of phosphorus is used in the head of the safety match, but it consists of an oxidizing agent ($Pb_3O_4$, $KClO_3$, $K_2Cr_2O_7$), antimony trisulfide, powdered glass and glue (or dextrin). These matches are ignited by rubbing them on a surface consisting of antimony trisulfide, red phosphorus, and glue. If the so-called safety match is dry and is drawn quickly over glass, slate, etc., it can be ignited.

## BINARY COMPOUNDS OF PHOSPHORUS

**542. Phosphine, $PH_3$.**—Hydrogen phosphide or phosphine, $PH_3$, can be prepared by the hydrolysis of phosphides (compare hydrolysis of nitrides, Demonstration 104):

$$Ca_3P_2 + 6HOH \rightarrow 3Ca(OH)_2 + 2PH_3 \uparrow .$$

### DEMONSTRATION 141. PHOSPHINE RINGS

Materials: Set-up in Fig. 173; white P; KOH; illuminating gas or hydrogen. (CARE: *illuminating gas must first be passed into the flask to displace oxygen and prevent explosion.*)

Phosphine may also be prepared by the interaction of phosphorus and potassium hydroxide (See equation in Fig. 173). The bubbles of $PH_3$ ignite spontaneously, forming smoke rings of phosphoric acid, $H_3PO_4$. (Write the equation.)

Phosphine is a colorless, poisonous gas with a disagreeable odor, like that of rotten fish. It is analogous to ammonia, but is less strongly basic. Thus, it combines with HI to form **phosphonium iodide**, a compound somewhat similar to ammonium iodide and ammonium chloride:

$$PH_3 + HI \rightleftarrows PH_4I,$$
$$NH_3 + HCl \rightleftarrows NH_4Cl.$$

The phosphonium ion, $PH_4^+$, is even more unstable than the ammonium ion, $NH_4^+$; so that $PH_4I$ dissociates at a lower temperature than $NH_4Cl$.

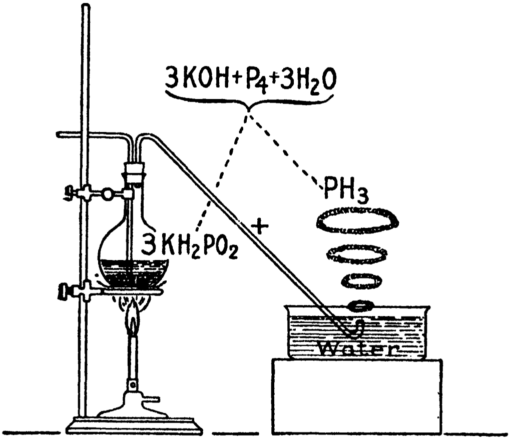


FIG. 173. Smoke rings of $P_2O_5$ from the spontaneous ignition of $PH_3$ in air

**543. Halides of Phosphorus.**—White phosphorus burns in dry chlorine gas to form **phosphorus trichloride,** $PCl_3$; or, when chlorine is in excess, **phosphorus pentachloride,** $PCl_5$. Other halides are similarly formed. $PF_3$ and $PF_5$ are gases; $PCl_3$ and $PBr_3$ are liquids; while $PCl_5$, $PBr_5$ and $PI_3$ are solids.

### DEMONSTRATION 142. THERMAL DISSOCIATION OF $PBr_5$

Materials: Two sealed pyrex tubes containing solid $PBr_5$; one clamped over burner.

Phosphorus pentahalides dissociate into trihalides upon heating. This may be shown by heating one of the tubes, which thereupon becomes reddish brown. The color disappears as the tube cools down to room temperature:

$$\underset{\text{colorless}}{BPr_5} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftarrows}} \underset{\text{colorless}}{PBr_3} + \underset{\text{reddish brown}}{Br_2}.$$

Above 300° $PCl_5$ is 97 per cent dissociated (216).

Phosphorus halides completely hydrolyze. Phosphorus trichloride forms phosphorus acid ($H_3PO_3$), whereas phosphorus pentachloride forms phosphorus oxychloride or, with excess water, phosphoric acid:

$$\begin{aligned} PCl_3 + 3HOH &\rightarrow 3HCl + H_3PO_3, \\ PCl_5 + H_2O &\rightarrow POCl_3 + 2HCl, \\ PCl_5 + 4H_2O &\rightarrow H_3PO_4 + 5HCl. \end{aligned}$$

DEMONSTRATION 143. HYDROLYSIS OF HALIDES OF GROUP V-B

Materials: $PCl_5$, $SbCl_3$, $AsCl_3$, $Bi(NO_3)_3$; 4 test glasses.

When the three halides are diluted with water, white precipitates of oxy-chlorides are formed, *e.g.*, POCl, SbOCl, AsOCl. Bismuth nitrate forms bismuth subnitrate, $Bi(OH)_2NO_3$.

**544. Oxides of Phosphorus.**—Phosphorus forms three oxides:

TABLE 108

| OXIDE | | (ANHYDRIDE OF) |
|---|---|---|
| phosphorus trioxide | $(P_2O_3)_2$ | (ous acid) |
| phosphorus tetroxide | $(P_2O_4)$ | |
| phosphorus pentoxide | $(P_2O_5)_2$ | (ic acid) |

The first and last are usually written as $P_2O_3$ and $P_2O_5$, although their vapor densities show them to have the formulas $P_4O_6$ and $P_4O_{10}$.

**Phosphorus trioxide** can be prepared as a wax-like mass or as feathery crystals by the slow oxidation of phosphorus. It has the odor of phosphorus

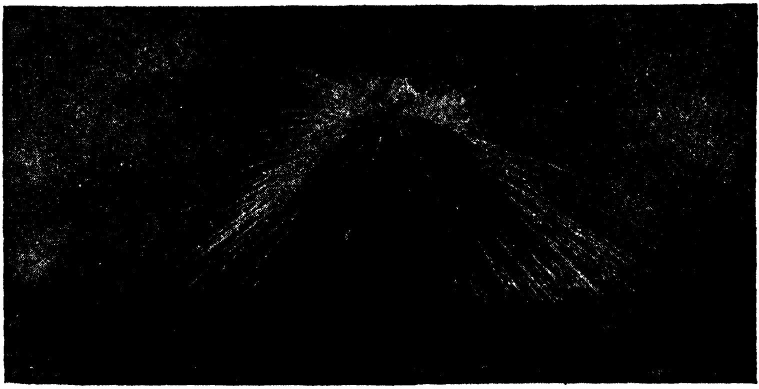


FIG. 174. Bursting phosphorous airplane bomb envelopes the ship in phosphorus pentoxide.

and is poisonous. This oxide melts at 22.5° and boils at 173°. The oxide dissolves slowly in cold water to form phosphorous acid; but with hot water a violent, complicated reaction takes place. When phosphorous oxide is heated to 440° it decomposes, yielding phosphorus tetroxide ($P_2O_4$) and red phosphorus.

**Phosphorus pentoxide** is readily obtained in the form of dense white clouds by burning phosphorus in excess of dry air or oxygen. The fumes may be easily condensed upon the sides of a cold vessel. The oxide may be obtained as a white flocculent powder or in the form of a glassy mass.

$P_2O_5$ may also be produced by heating a mixture of calcium phosphate and sand ($SiO_2$) in the electric furnace, the oxide being volatilized. The white fumes are then precipitated by the Cottrell electric process.

Phosphorus pentoxide has great affinity for water, and on account of this property it is one of the best dehydrating agents known.

### DEMONSTRATION 144. AFFINITY OF $P_2O_5$ FOR WATER

Materials: Small tuft of guncotton beside a pile of $P_2O_5$ on clock-glass; pipette.

When a drop of water is added, it is absorbed so quickly by the $P_2O_5$, and so much heat is suddenly given off, that the guncotton is ignited.

### OXY-ACIDS OF PHOSPHORUS

**545. Phosphorus Acid, $H_2(HPO_3)$.**—This acid may be prepared by the hydrolysis of phosphorus trichloride, or by the action of phosphorus trioxide on cold water:

$$P_2O_3 + 3H_2O \xrightarrow{\text{cold}} 2H_2(HPO_3).$$

The product is written in this peculiar form since ordinarily only two of its hydrogen atoms are replaced by metals, *i.e.*, $Na_2HPO_3$. Phosphorus acid is a crystalline solid which melts at 70.1°. It is a powerful reducing agent. Its salts are called **phosphites**.

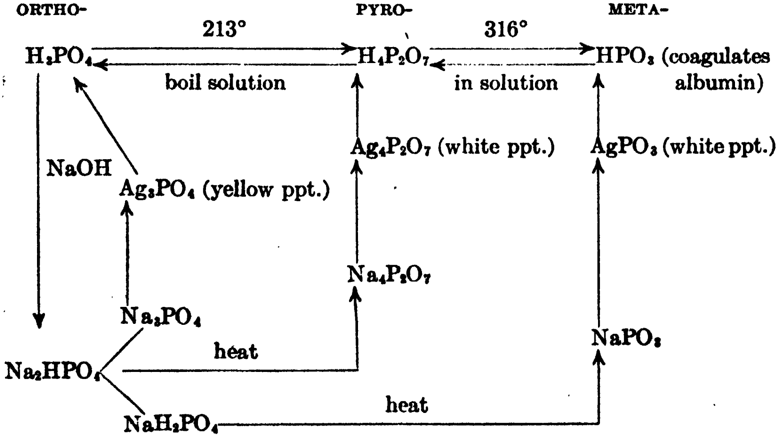


FIG. 175. Phosphoric acids and phosphates.

**546. Phosphoric Acids.**—The interrelations between **orthophosphoric, pyrophosphoric, and metaphosphoric acids,** and important salts of these acids, are shown in Fig. 175.

It should be noted in this connection that $P_2O_5$ is the anhydride of the three phosphoric acids; it is simply a matter of hydration.

$$\begin{aligned}&2HPO_3\ (=H_2O,\ P_2O_5),\\&H_4P_2O_7\ (=2H_2O,\ P_2O_5),\\&2H_3PO_4\ (=3H_2O,\ P_2O_5).\end{aligned}$$

**Orthophosphoric acid, $H_3PO_4$,** commonly called simply **phosphoric acid** (145), is the most important of these acids. It is made either (*a*) by treating calcium phosphate (either bone-ash or phosphate rock) with sulfuric acid, or (*b*) by burning phosphorus and dissolving the oxide in *hot* water:

(*a*) $$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4,$$

(*b*) $$P_4 + 5O_2 \rightarrow 2P_2O_5;\quad P_2O_5 + 3H_2O \xrightarrow{\text{hot}} 2H_3PO_4.$$

Orthophosphoric acid is a white, deliquescent solid, extremely soluble in water; the 85 per cent commercial solution has the consistency of syrup.

An aqueous solution of orthophosphoric acid is much weaker than sulfuric acid, but is stronger than acetic or boric acids. It ionizes as follows:

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^- \rightleftarrows 2H^+ + HPO_4^= \rightleftarrows 3H^+ + PO_4^\equiv,$$

that is, a solution contains chiefly $H_2PO_4^-$, little $HPO_4^=$, and practically no $PO_4^\equiv$.

**Pyrophosphoric acid, $H_4P_2O_7$,** obtained by heating orthophosphoric acid between 213° and 316°, is a colorless, glassy mass, which melts at about 61°. It dissolves in water to form $H_3PO_4$.

$$2H_3PO_4 \underset{\text{dissolve}}{\overset{\text{heat}}{\rightleftarrows}} H_4P_2O_7 + H_2O.$$

**Metaphosphoric acid, $HPO_3$** is obtained by heating the other phosphoric acids above 316°, or by dissolving $P_2O_5$ in *cold* water:

$$H_3PO_4 \xrightarrow{316°} HPO_3 + H_2O,$$

$$P_2O_5 + H_2O \xrightarrow{\text{cold}} 2HPO_3.$$

Metaphosphoric acid is prepared in the form of white, deliquescent sticks (the "glacial phosphoric acid" of commerce). It is soluble in cold water with which it combines ultimately to form phosphoric acid. By boiling the solution, $H_3PO_4$ is formed quickly.

Metaphosphoric acid coagulates albumin (white of egg suspended in water), whereas ortho- and pyrophosphoric acids do not.

**547. Phosphates.**—Salts of the foregoing three phosphoric acids are called **phosphates.**

### DEMONSTRATION 145. REACTIONS OF PHOSPHATES

Materials: (*a*) Solutions of $Na_2HPO_4$, $MgSO_4$, $AgNO_3$, $NH_4OH$; (*b*) Pt wire for bead tests; microcosmic salt ($NaNH_4HPO_4$), $CoCl_2$, $FeCl_2$, $CuCl_2$; (*c*) egg albumin, sodium metaphosphate; (*d*) sodium pyrophosphate.

Some of the characteristic reactions given in Fig. 175, or described below, may be confirmed.

**a. Orthophosphates** form primary, secondary and tertiary salts; the hydrolysis of these in water is indicated in Table 109.

TABLE 109. ORTHOPHOSPHATES IN WATER

| SALT | CLASS | HYDROLYZES AS FOLLOWS (ONLY ANION INDICATED) | REACTION TO LITMUS |
|---|---|---|---|
| $NaH_2PO_4, H_2O$ | primary | $H_2PO_4^-$ | weakly acidic |
| $Na_2HPO_4, 12H_2O$ | secondary | $HPO_4^= + HOH \rightarrow H_2PO_4^- + OH^-$ | basic |
| $Na_3PO_4, 12H_2O$ | tertiary | $PO_4^{\equiv} + 2HOH \rightarrow H_2PO_4^- + 2OH^-$ | strongly basic |

Their reaction to litmus is a consequence of the rule (**546**) that $H_2PO_4^-$ predominates in aqueous solutions.

Sodium ammonium hydrogen phosphate, or *microcosmic salt*, $Na(NH_4)HPO_4, 2H_2O$ is a white crystalline orthophosphate excreted in the urine.

Important analytical reactions of orthophosphates (Fig. 175 and Demonstration 145) are:

$$Na_2HPO_4 + 3AgNO_3 \rightarrow \underset{\text{yellow}}{Ag_3PO_4} + 2NaNO_3 + HNO_3,$$

$$5H_2O + NH_4OH + Mg^{++} + HPO_4^= \rightarrow NH_4MgPO_4, 6H_2O.$$

In the first, the $HNO_3$ must be neutralized to complete precipitation. The second reaction is used in quantitative analysis to estimate both magnesium and phosphoric acid.

**b. Pyrophosphates** may be prepared by heating secondary phosphates:

$$2Na_2HPO_4 \rightleftarrows Na_4P_2O_7 + H_2O.$$

Ammonium magnesium phosphate, when heated, yields *magnesium pyrophosphate*, a very stable salt:

$$2NH_4MgPO_4 \rightarrow Mg_2P_2O_7 + 2NH_3 + H_2O.$$

**c. Metaphosphates** may be obtained by heating primary orthophosphates:

$$NaH_2PO_4 \rightleftarrows NaPO_3 + H_2O.$$

When microcosmic salt is heated to a high temperature, *sodium metaphosphate* is formed:

$$NaNH_4HPO_4 \rightarrow NaPO_3 + NH_3 + H_2O.$$

This salt is used by chemists and mineralogists as a test for certain metallic oxides. A bead is prepared by heating a little microcosmic salt on the end of a platinum wire. When minute quantities of certain metallic oxides are heated in contact with the beads in the flame of a burner, characteristic colors are obtained. Thus cobalt oxide colors the bead blue:

$$NaPO_3 + CoO \rightarrow NaCoPO_4 \text{ (blue bead)}.$$

**548. Superphosphate Fertilizers.**—The consumption of phosphorus by plants gradually depletes the soil, and it is necessary to add phosphate fertilizers to make up for this deficiency. The salt generally used is **primary calcium phosphate, $Ca(H_2PO_4)_2$,** which is sold under the technical name **superphosphate.**

According to T. M. Lowry, the pasture lands of England became greatly impoverished a century ago, on account of the removal of phosphorus; but the fertility of the soil was restored by manuring it with bones gathered from the battlefields of Europe.

Tertiary calcium phosphate, $Ca_3(PO_4)_2$, which is in phosphate rock and bones, is insoluble and cannot be used. However, it is converted into a soluble plant-fertilizer by treatment with sulfuric acid, a process discovered in 1840 by Sir John Laws. Nearly half of the sulfuric acid output of the world is used for the following reaction:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O \rightarrow \underbrace{\underset{\text{superphosphate}}{Ca(H_2PO_4)_2} + \underset{\text{gypsum}}{2CaSO_4, 2H_2O}}_{\textbf{superphosphate of lime}}.$$

The world's consumption of phosphate rock for fertilizer is enormous. Practically all of the rock comes from the United States and Northern Africa.

Thus, in 1939 Morocco produced 1,447,544 metric tons, Nauru and the Ocean Islands 1,184,816 tons, Tunisia 1,934,200 tons and the United States 3,799,253 tons. Of the latter, 2,678,784 tons came from Florida. The remainder of the world produced less than 2,000,000 tons. Tennessee, South Carolina and Montana follow in that order. A three-billion ton reserve of phosphate rock analyzing 30 per cent $Ca_3(PO_4)_2$ has been uncovered in Utah, Montana, Wyoming and Idaho.

Germany is lacking in phosphates: it produced only 3221 tons in 1938, and obtained 70 per cent of its phosphate fertilizer from basic Bessemer slag (**429**); it produced 2,550,000 tons of phosphate fertilizer in 1938 from this latter source.

## ARSENIC $^{74.91}_{33}As$

**549. Occurrence and Preparation.**—The ancients were acquainted with arsenic (As), with "white arsenic" ($As_2O_3$) and with the naturally occurring red and yellow sulfides of arsenic, red **realgar** ($As_2S_2$) and yellow **orpiment** ($As_2S_3$).

Arsenic sulfides are associated with sulfide ores of lead, nickel, zinc, copper, gold and silver, usually as arsenopyrite, FeAsS, called **mispickel.** During the smelting of these sulfide ores, arsenic trioxide is formed; it volatilizes, and may be precipitated from the flue-dusts (section 669, Fig. 225). Flue dusts may contain 30 per cent $As_2O_3$. The arsenic compounds made from this are therefore a by-product of the smelting furnaces.

World consumption is approximately 50,000 tons of arsenic yearly; in 1939, the United States supplied 20,267 tons and Mexico 8,063, while France and Germany accounted for 5,000 tons each.

Arsenic may be prepared also by heating *arsenopyrite,* the air being excluded:

$$4FeAsS \rightarrow 4FeS + As_4 \uparrow.$$

The arsenic sublimes into iron tubes, and is obtained as a brittle, crystalline mass having a metallic appearance.

In the laboratory it may be obtained by heating the oxide with carbon in a hard-glass test-tube. This method, employing iron crucibles, is used commercially in Silesia:

$$2As_2O_3 + 6C \rightarrow 6CO + As_4 \uparrow.$$

**550. Properties.**—Arsenic is a brittle, steel-gray, crystalline solid having the appearance of a metal. Its specific gravity at 14° is 5.727. Allotropic forms of arsenic are known, however, so its density is variable. When arsenic is heated under ordinary conditions, it forms a vapor without melting. The vapor is of a lemon-yellow color and has the odor of garlic. At 644° the vapor consists of tetratomic molecules ($As_4$), but at 1,700° the molecules are diatomic ($As_2$).

Arsenic combines with many elements. Heated with metals it forms **arsenides,** corresponding to nitrides and phosphides. Heated with the halogens or with sulfur it forms arsenic or arsenious compounds. Arsenic burns in air or oxygen with a white flame, forming arsenic trioxide. Chemically, arsenic closely resembles phosphorus.

Arsenic is used for hardening metals, particularly in manufacturing lead shot.

### COMPOUNDS OF ARSENIC

**551. Arsine, or Hydrogen Arsenide, $AsH_3$.**—This compound is analogous to ammonia and phosphine. It is unstable, for upon heating it, arsenic is formed.

This is the basis of an exceedingly delicate test for arsenic known as the **Marsh test.** (Fig. 176.)

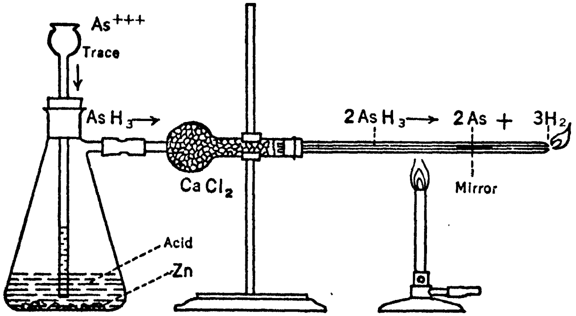


FIG. 176. The Marsh Test for arsenic.

### DEMONSTRATION 146. THE MARSH TEST

Materials: Solutions of $AsCl_3$, $SbCl_3$, and HCl; granulated zinc, burner; set-up in Fig. 176.

In an analysis of the stomach of a person suspected to have been poisoned by arsenic, the finely-ground matter is placed in a hydrogen generator containing zinc and hydrochloric acid. Arsine is evolved, is dried by passing it through calcium chloride, and is finally passed through a heated tube. Here dissociation occurs, and a steel-grey mirror of arsenic is deposited further along the tube, where it is cooler. The chemical changes are indicated in the figure.

Arsine is very poisonous! Great care must be exercised in preparing this gas. Gehlen, in 1815, lost his life by breathing an exceedingly small amount of it. Arsine has a peculiar and disagreeable odor. *Unlike* $NH_3$ *and* $PH_3$ *it forms no compounds with halogen acids.*

Certain arsenides also tend to hydrolyze, forming arsine. This action may be compared with that of water upon phosphides (*e.g.*, $Ca_3P_2$) and nitrides (*e.g.*, $Mg_3N_2$).

**552. Oxides of Arsenic.**—Arsenic forms two common oxides: arsenious oxide, $As_2O_3$, and arsenic pentoxide, $As_2O_5$.

**Arsenious oxide** or **arsenic trioxide**, the most important compound of arsenic, is often called "white arsenic," or simply "arsenic." Its vapor density up to 1,500° shows that its formula is $As_4O_6$, but the simpler formula $As_2O_3$ is generally used. As described above, it is a by-product from the flue-dusts of sulfide smelters.

From the position of arsenic in the Periodic Table (*q.v.*) we should expect $As_2O_3$ to be **amphoteric.** This is confirmed by the following reactions; in the first $As_2O_3$ behaves like the oxide of a metal (compare, CaO), while in the second it resembles the oxide of a non-metal (compare $CO_2$):

$$As_2O_3 + 6HCl \rightarrow 3H_2O + \underset{\text{arsenic trichloride}}{2AsCl_3},$$

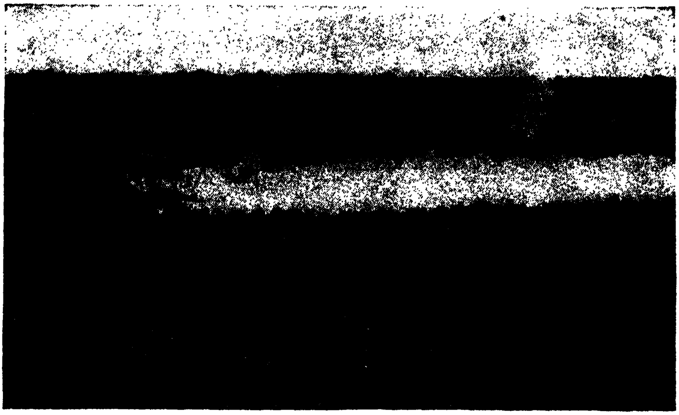
$$As_2O_3 + 6NaOH \rightarrow 3H_2O + \underset{\text{sodium arsenite}}{2Na_3AsO_3}.$$

Arsenic trioxide is poisonous, and is used as an insecticide either as "white arsenic" or as one of the salts of arsenic; these insecticides accounted for 88 per cent of the arsenic produced in 1939.

There were 33,913 tons of "white arsenic," approximately 25,000 tons of lead arsenate, and about 15,000 tons of calcium arsenate used as insecticides in 1939 in the United States. The Federal Government itself appropriated $5,000,000 for this purpose, and consumed 1,536,000 gallons of a solution of sodium arsenite in combating grasshoppers, 338,000 pounds of dry sodium arsenite for Mormon crickets, and 420,000 pounds of calcium arsenite and 84,000 gallons of a solution of sodium arsenite for white-fringed beetles.

Although 4 grains of white arsenic is usually fatal, woodcutters have been known to accustom themselves to daily doses as large as this; they claim that use of the substance enables them to carry heavy loads with ease. In fact, the word *arsenic* comes from the Greek, meaning *masculine* or *potent.*

The poisonous properties of arsenic compounds attracted the attention of Ehrlich in his quest for a specific poison to kill trypanisomes and, later, syphillis germs; and as a result of his successful research, 12,390,837 doses of arsenical drugs were administered in the United States in 1939.



*Courtesy of the Department of Agriculture, Bureau of Entomology and Plant Quarantine*

FIG. 177. Dusting calcium arsenite in combatting cotton boll weevil.

**Arsenic pentoxide,** $As_2O_5$, may be obtained as a white porous mass by heating arsenic acid to a temperature slightly below redness:

$$2H_3AsO_4 \rightleftarrows 3H_2O + As_2O_5.$$

The pentoxide interacts with water to form arsenic acid.

**553. Sulfides of Arsenic.**—**Arsenic disulfide,** $As_2S_2$, occurs as the mineral *realgar.* It can be prepared as a red, vitreous mass by fusing together arsenic and sulfur. $As_2S_2$ is employed in the manufacture of "white-fire," or "Bengal Lights," and in tanning.

T. L. Shear discovered in the excavations at Corinth, a crude pot containing a red pigment, found to be realgar. Objects lying in the vicinity of the pot belong to the end of the fifth or the beginning of the fourth century B.C.

**Arsenic trisulfide,** $As_2S_3$, occurs in nature as the mineral *orpiment.* It can be prepared as a fine yellow precipitate by passing hydrogen sulfide into a solution of $As_2O_3$ in hydrochloric acid:

$$2AsCl_3 + 3H_2S \rightarrow As_2S_3 \downarrow + 6HCl.$$

The compound is insoluble in water. When $As_2O_3$ is dissolved in water and then treated with pure hydrogen sulfide, a liquid with a yellow color is obtained. Arsenic trisulfide is formed, but is present in colloidal form; it may be coagulated by adding an acid to the liquid.

**Arsenic pentasulfide,** $As_2S_5$, can be obtained as a yellow precipitate by saturating a strong hydrochloric acid solution of quinquivalent arsenic, kept cold, with a rapid stream of $H_2S$:

$$2H_3AsO_4 + 5H_2S \rightarrow As_2S_5 \downarrow + 8H_2O.$$

**554. Other Arsenic Compounds.**—Arsenic forms a number of oxy-acids. **Arsenious acid**, $H_3AsO_3$, corresponds to, but is weaker than, phosphorous acid. Its salts, called **arsenites**, are used as insecticides. This includes sodium arsenite (552), **Paris green** (a double salt of copper arsenite and acetate), and **Scheele's green**, $CuHAsO_3$.

**Arsenic acids** corresponding to, but weaker than, phosphoric acids are $H_3AsO_4$, arsenic acid; $H_4As_2O_7$, pyroarsenic acid; and $HAsO_3$, metarsenic acid. Arsenic acid is stronger than arsenious acid, just as nitric acid is stronger than nitrous acid; *i.e.*, **the oxy-acid in which the element has the highest positive valence is always strongest.** Salts of orthoarsenic acid are called orthoarsenates, or simply **arsenates.** The use of lead arsenate and calcium arsenate as insecticides has already been mentioned (552). The formation of a reddish brown precipitate of **silver arsenate**, $Ag_3AsO_4$, is an analytical test for arsenates.

In **routine qualitative analysis**, arsenic sulfides are separated from sulfides of the copper group by treating with yellow ammonium sulfide, $(NH_4)_2S_5$, (actually $(NH_4)_2S_x$); in this case soluble **ammonium thioarsenate** is formed:

$$As_2S_3 + 3(NH_4)_2S_5 \rightarrow 2(NH_4)_3AsS_4 + 10S,$$
$$As_2S_5 + \underset{\text{ammonium polysulfide}}{3(NH_4)_2S_5} \rightarrow \underset{\text{ammonium thioarsenate}}{2(NH_4)_3AsS_4} + 12S.$$

Subsequently, upon treating the solution of thioarsenate with acid, arsenic pentasulfide is precipitated:

$$2(NH_4)_3AsS_4 + 6HCl \rightarrow 6NH_4Cl + 3H_2S \uparrow + As_2S_5 \downarrow .$$

**Thioarsenites** are also known; *e.g.*, ammonium thioarsenite, $(NH_4)_3AsS_3$, is obtained when arsenic trioxide is treated with ammonium sulfide.

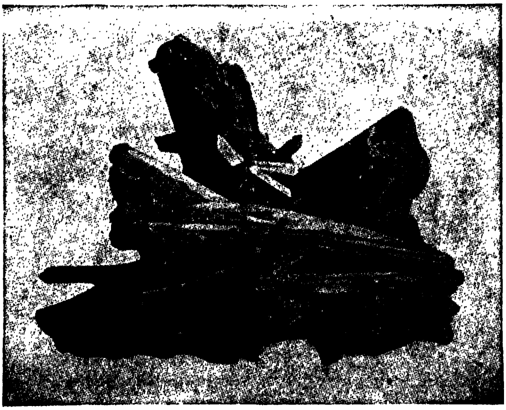


FIG. 178. Antimony glance, $Sb_2S_3$.

### ANTIMONY $^{121.76}_{51}Sb$

**555. History and Occurrence.**—Antimony occurs in nature chiefly as the mineral **stibnite** or **antimony glance,** $Sb_2S_3$ (Fig.

178). This compound was used in very early times by Oriental women for painting the eyebrows. Paracelsus and other iatrochemists were acquainted with many preparations containing antimony. Indeed, the use of antimony in medicine was quite the vogue in the days of the medical chemists. A book entitled the "*Triumphal Chariot of Antimony*" was published at an early date.

China formerly produced 80 per cent of all the antimony consumed; but by 1939 production had shifted to Central and South America. In that year Bolivia accounted for 29 per cent, Mexico 23 per cent, China 20 per cent and Yugoslavia 10 per cent. The United States, which produced only 1 per cent, consumed 92 per cent of the world total.

**556. Preparation.**—Antimony may be prepared in two ways:

(*a*) By roasting stibnite and then reducing the oxide with carbon. The reduction is carried out in graphite crucibles:

$$\begin{aligned} Sb_2S_3 + 5O_2 &\rightarrow Sb_2O_4 + 3SO_2, \\ Sb_2O_4 + 4C &\rightarrow 2Sb + 4CO. \end{aligned}$$

(*b*) By reducing stibnite with iron. Graphite crucibles are also employed in this method:

$$Sb_2S_3 + 3Fe \rightarrow 2Sb + 3FeS.$$

The crude metal separates from the slag (chiefly FeS) and is purified by heating with a small quantity of clean stibnite.

**557. Properties.**—Antimony is a hard, brittle, silver-white crystalline solid, having a specific gravity of 6.7 and a melting point of 630°. At 1,640° the molecular formula is $Sb_2$, but at lower temperatures, $Sb_4$ is present. Antimony has allotropic forms, the most peculiar and interesting of which is "explosive antimony"; it may be obtained by the electrolysis of a solution of antimony trichloride. When this form of antimony is heated to 200°, it explodes sharply, forming a fine powder; it also breaks down when scratched with a metallic point or when touched with a red-hot wire.

When antimony is heated in air, it burns with a bluish flame, forming oxides. A small globule of molten antimony thrown upon a piece of paper breaks into tiny globules, each of which skips about on the paper, burning all the while, and leaving very regularly marked hyperbolic trails. Antimony also combines directly with the halogens. As might be expected from its position in the Periodic Table, antimony is amphoteric, being somewhat more metallic then arsenic.

### COMPOUNDS OF ANTIMONY

**558. Stibine, $SbH_3$.**—Antimony hydride, like arsine gives an antimony mirror when treated by the Marsh test (551). The mirror, unlike that for arsenic, does not volatilize in the Bunsen flame, and is insoluble in a solution of bleaching powder.

**559. Oxides of Antimony.**—These are analogous to the oxides of arsenic. **Antimony trioxide** is obtained as a white powder upon heating antimony or its sulfide in air, or upon treating antimony with nitric acid. **Antimony pentoxide** is obtained as a light yellow powder upon evaporating a mixture of Sb (or $Sb_2O_3$) and nitric acid to dryness. **Antimony tetroxide,** $Sb_2O_4$, is a white powder formed when either of the other oxides is heated to a high temperature in the presence of air. It is probably antimony antimonate, *i.e.*, $Sb(SbO_4)$.

**560. Other Compounds of Antimony.**—

**a. Oxy-acids.** Antimony forms antimonious acid, ($H_3SbO_3$), and antimonic acid, $H_3SbO_4$, corresponding to analogous acids formed by other members of the V-B group.

**b. Halides.** Halides of the type $SbX_3$ and $SbX_5$, like other salts of antimony, are partially hydrolyzed by water:

$$\underset{\text{antimony trichloride}}{SbCl_3} + H_2O \rightarrow 2HCl + \underset{\text{antimony oxychloride}}{SbOCl}.$$

Antimony trichloride is produced by heating antimony or stibnite in dry chlorine. It is used to give a brown stain to iron and steel wares, such as gun-barrels.

**c. Sulfides.** Antimony trisulfide, $Sb_2S_3$, which occurs in nature as stibnite, is precipitated in routine chemical analysis. The pentasulfide $Sb_2S_5$, is formed when a thioantimonate is treated with acid (compare arsenic, 554). $Sb_2S_5$ resembles the trisulfide, but is unstable.

**d. The antimonyl radical** (SbO). This radical is present in a number of salts of antimony. It occurs in **tartar emetic,** antimonyl potassium tartrate, $(SbO)KC_4H_4O_6, \frac{1}{2}H_2O$, a medicinal used as a heart depressant.

**561. Uses of Antimony.**—Antimony forms hard alloys with most heavy metals; the property of these alloys to expand upon cooling makes them suitable for **type metal** (Sb-Pb-Sn) and

**Britannia metal** (Sb-Sn-Cu-Zn), the latter being used in making cheap tableware. Another important alloy of antimony is **Babbitt metal** (Sb-Sn-Cu), used to reduce friction in bearings; 11,785 tons of antimony was consumed domestically for this purpose in 1939.

Between 4 and 12 per cent of antimony is used in the lead plates of storage batteries; 106,500 tons of antimony was needed in the United States for this in 1939.

Antimony compounds accounted for only 6188 tons in 1939. Sulfides are used in safety matches, cartridge primers, and as a red pigment in paint and red rubber. $Sb_2O_4$ is employed in the manufacture of opaque white enamels.

### BISMUTH ${}^{209.0}_{83}Bi$

**562. Occurrence and Preparation.**—Bismuth was known in the Middle Ages. It is not abundant, but it is widely scattered in the free state in many countries, including Bolivia, Germany, Peru, Chile and the United States. Minerals such as bismuth glance, $Bi_2S_3$, and bismuth ochre, $Bi_2O_3$, are also found. Today considerable quantities of bismuth are obtained from by-product concentrates from copper and lead smelters, and from tin ores mined in Bolivia. About 1000 tons are produced each year. The concentrates are usually stored, and treated a year or two later when demand for bismuth is heavy.

Bismuth is prepared by roasting the sulfide in a furnace, and then reducing the oxide with carbon:

$$2Bi_2O_3 + 3C \rightarrow 4Bi + 3CO_2.$$

**563. Properties.**—Bismuth is a shiny, brittle, gray-white crystalline metal with a ruddy tint. It has a specific gravity of 9.8, and melts at 271°. Bismuth is a poorer conductor of heat and electricity than is any other metal; it is approximately 100 times less conductive than silver. Bismuth is also the most diamagnetic substance known.

Heated in air, bismuth burns to form $Bi_2O_3$. Unlike other members of the phosphorus family, bismuth is exclusively metallic in character, and forms no acids. Bismuth dissolves in hot concentrated nitric and sulfuric acids forming bismuth nitrate $Bi(NO_3)_3$ and bismuth sulfate, $Bi_2(SO_4)_3$.

**564. Compounds of Bismuth.**—

**a. Oxides.** Bismuth forms the monoxide, BiO, and also oxides corresponding to $Sb_2O_3$ and $Sb_2O_5$. The trioxide is obtained as a yellow powder by oxidizing the metal or by heating the nitrate or hydroxide. $Bi_2O_3$ is more basic than $Sb_2O_3$.

**b. Sulfides.** BiS and $Bi_2S_3$ are known. The trisulfide may be produced as a brown-black precipitate by treating a solution of bismuth salt with hydrogen sulfide. The compound is soluble in hot dilute nitric acid, but insoluble in the sulfides of ammonium (see Arsenic and Antimony).

**c. Halides, nitrate, etc.** These salts, like those of antimony, undergo partial hydrolysis in water. Thus, when a few drops of a solution of bismuth chloride are poured into a beaker of water, a white precipitate of bismuth oxychloride forms:

$$BiCl_3 + H_2O \rightleftarrows BiOCl \downarrow + 2HCl.$$

**d. Bismuthyl radical, BiO.** Corresponding to the *antimonyl radical* (**560, d**), bismuth forms the radical BiO which enters into a number of compounds. For instance, bismuthyl nitrate, $(BiO)NO_3$, is formed when bismuth subnitrate, $Bi(OH)_2NO_3$, is heated and dried.

**565. Uses of Bismuth.** About 90 per cent of the domestic bismuth consumption is by the pharmaceutical trade, principally for intestinal and stomach remedies. These include the subcarbonate, subnitrate, subsalicylate, subgallate, etc., salts of bismuth. Also, bismuth carbonate and the basic nitrate are consumed in connection with the X-ray examination of the oesophagus and stomach. Bismuth is nearly opaque to X-rays, owing to its high atomic weight.

Bismuth metal is consumed in making low-melting alloys. This use illustrates the general rule that an alloy has a lower melting point than its constituent metals. Thus **Woods' metal**, which contains 4 parts of Bi, 2 parts of Pb, 1 part of tin, and 1 part cadmium melts at 60.5°; and **Rose's metal** which contains 2 parts of Bi, 1 part of Pb and 1 part of Sn melts at 93.8°. These fusible alloys are used in the manufacture of safety plugs in boilers, automatic fire curtains, water-sprinklers, etc.

### DEMONSTRATION 147. LOW-MELTING ALLOYS

Materials: Rod of Woods' metal clamped over a 250 cc. Erlenmeyer flask ½ full of water, and over burner.

When steam issues from the mouth of the flask, the Woods' metal melts and drips down.

## QUESTION REVIEW

**The nitrogen family (537).**

1. Compare and contrast the members of group V-B.

I. PHOSPHORUS.

**a. Occurrence (538). Preparation (539). Properties (540).**

2. How much coke is consumed in producing 1 ton of phosphorus? Why is the Monsanto plant located in the Tennessee Valley?
3. Contrast the properties of white phosphorus with those of the red allotropic form.

**b. Matches (541).**

4. Show by equations what happens during the lighting of a safety match.

**c. Binary compounds: phosphine (542); halides (543); oxides (544).**

5. Give equations illustrating (*a*) a comparison between phosphine and ammonia, (*b*) hydrolysis, (*c*) thermal dissociation, (*d*) acid anhydrides.
6. Is the dissociation of phosphorus pentabromide an exothermic or an endothermic reaction?

**d. Oxy-acids of phosphorus (545–546).**

7. By means of equations show the preparation of the oxy-acids of phosphorus. State one important fact about each.
8. How would you distinguish an orthophosphate from a metaphosphate? A pyrophosphate from an orthophosphate?

**e. Phosphates (547). Superphosphate fertilizers (548).**

9. Why is tertiary sodium phosphate more basic than the secondary salt?
10. Explain the use of microcosmic salt in analysis. What other substance forms "beads" (465, b)?
11. From what source does Germany obtain its phosphate fertilizer? Give equations.
12. Differentiate between "superphosphate" and "superphosphate of lime."

II. ARSENIC (549–554).

13. Explain the statement that "arsenic is a by-product."
14. Calculate the weight of 1 liter of arsenic vapor at 700° C.

15. Diagram the Marsh-test apparatus, giving equations.
16. Give equations to show that arsenic pentoxide is amphoteric.
17. Show, by an equation, the formation of a thioarsenate in separating arsenic from copper in qualitative analysis.

III. ANTIMONY (555–561).

18. Repeat questions 15, 16 and 17, substituting antimony for arsenic. Indicate any differences between the two elements.
19. State one important fact about: $SbOCl$, $Sb_2O_4$, $Sb_2S_3$, and $(SbO)$.
20. State the chief uses for antimony.

IV. BISMUTH (562–565).

21. Contrast the chemistry of bismuth with that of phosphorus.
22. Why do the production statistics for bismuth fluctuate widely from year to year?
23. State a use for (*a*) bismuth metal (*b*) a compound of bismuth.

**Reading References:** Articles number 13, 77, 230, 244, 308, 330 and 338 in the Appendix.

# CHAPTER XXXVIII

## THE SULFUR FAMILY. HYDROGEN SULFIDE

**566. General Characteristics of Group VI-B.**—The members of the sulfur family are sulfur, selenium, and tellurium. Group VI-B also includes oxygen and the rare, radioactive element polonium (**246**); but these are not included in the following discussion of the sulfur family. Table 110 summarizes the properties of the family.

TABLE 110. THE SULFUR FAMILY

| | SULFUR, S | SELENIUM, Se | TELLURIUM, Te |
|---|---|---|---|
| Atomic weight | 32.06 | 78.96 | 127.61 |
| Atomic number | 16 | 34 | 52 |
| Electronic arrangement | 2–8–6 | 2–8–18–6 | 2–8–18–18–6 |
| Melting point | 112.8°; 119° | 217° | 452° |
| Boiling point | 444.6° | 688° | 1390° |
| Density (solid) | 1.95–2.07 | 4.26–4.80 | 6.015–6.27 |
| Color of solid | Yellow | Reddish-brown | Silver-gray to black |
| Hydrides $XH_2$ | $H_2S$ | $H_2Se$ | $H_2Te$ |
| Oxides | $SO_2$<br>$SO_3$ | $SeO_2$<br>$SeO_3$ | $TeO_2$<br>$TeO_3$ |
| Oxygen acids | $H_2SO_3$<br>$H_2SO_4$ | $H_2SeO_3$<br>$H_2SeO_4$ | $H_2TeO_3$<br>$H_2TeO_4$ |

Sulfur, selenium and tellurium are all solids at room temperature. There is a gradual transition in physical properties as we proceed from the lightest to the heaviest member of the family. One common characteristic of these three elements is their existence in a number of allotropic forms.

From the table it is apparent that the common valences for the sulfur family are −2, +4, and +6, although all the valences between +1 and +6 are exhibited. The hydrides, $H_2S$, $H_2Se$, and $H_2Te$, are all colorless, poisonous gases with disagreeable odors; and the aqueous solutions of these hydrides are weak acids.

All three elements burn with oxygen to form dioxides, which dissolve in water to form *ous*-acids (*e.g.*, selenious acid, $H_2SeO_3$). The dioxides may be oxidized to trioxides, which dissolve in water to form *ic*-acids (*e.g.*, telluric acid, $H_2TeO_4$). Salts of these acids are similar in properties; $Ag_2S$, $Ag_2Se$ and $Ag_2Te$, for example, occur together in nature.

## SULFUR $^{32.06}_{16}S$

**567. History and Occurrence.**—Since sulfur occurs in the free state, it was one of the few elements known to the ancients. It was formerly called "brimstone." Sulfur was burned in ancient times for the purpose of fumigation.

### DEMONSTRATION 148. FORMATION OF SULFUR

Materials: Glass cylinders containing $H_2S$ and $SO_2$ respectively.

The precise way in which native sulfur is formed is not known. Volcanic gases, such as those of Vesuvius and of Mount Aetna generally contain sulfur dioxide and hydrogen sulfide, and when their moist gases interact sulfur is formed:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O.$$

The formation of sulfur by this reaction may be shown by bringing the mouths of the two cylinders together.

Sulfur in the petroleum fields of Texas and Louisiana was formed in a somewhat different manner, possibly by the interaction of calcium sulfate with methane gas found present in oil-bearing vicinities:

$$\underset{\text{anhydrite}}{2CaSO_4} + O_2 + \underset{\text{methane}}{2CH_4} \rightarrow \underset{\text{calcite}}{2CaCO_3} + 2S + 4H_2O.$$

The formation of sulfur in accordance with the foregoing reaction is only a theory; but the fact that calcite and sulfur usually occur together, while anhydrite is found in a lower layer (Fig. 179) lends support to this theory.

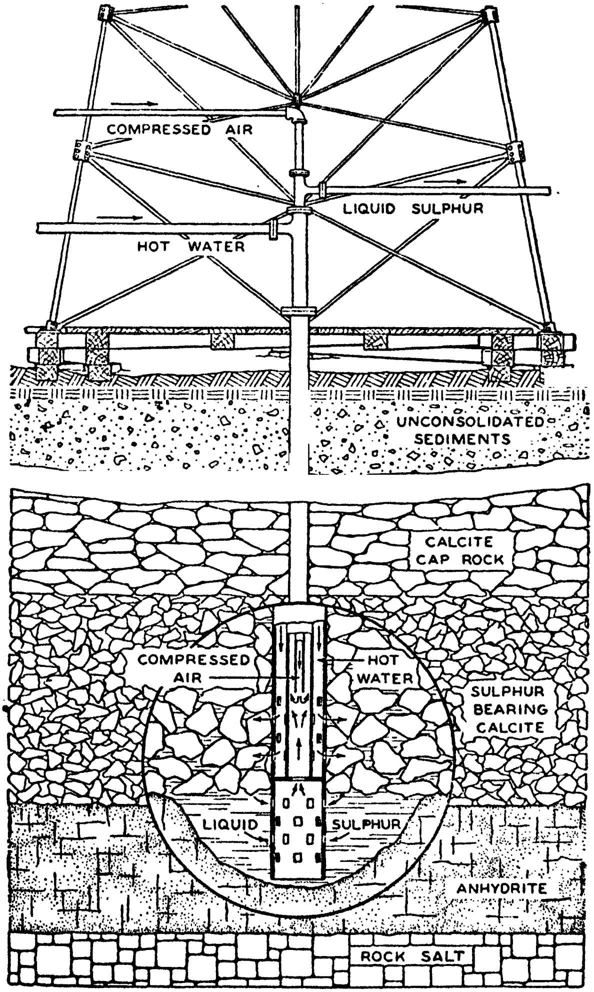
Sulfur in the combined state is much more abundant and widely distributed than is native sulfur. Some of the more important ores are given in Table 111.

TABLE 111. IMPORTANT ORES CONTAINING SULFUR

| Sulfides | | Sulfates | |
|---|---|---|---|
| Iron pyrites | $FeS_2$ | Gypsum | $CaSO_4, 2H_2O$ |
| Galena | $PbS$ | Anhydrite | $CaSO_4$ |
| Zinc blende | $ZnS$ | Celestite | $SrSO_4$ |
| Chalcopyrite | $CuFeS_2$ | Barite | $BaSO_4$ |
| Cinnabar | $HgS$ | Epsom salt | $MgSO_4, 7H_2O$ |
| Stibnite | $Sb_2S_3$ | Kieserite | $MgSO_4, H_2O$ |

Hydrogen sulfide gas is dissolved in the so-called "sulfur waters" and is present in volcanic gases.

Sulfur is an essential constituent in living matter. About 1 per cent is present in all abuminous substances. Its presence in petroleum and in coal annoys the industrialist, who finds his catalysts poisoned.



*Courtesy of the Texas Gulf Sulphur Company*

FIG. 179. The Frasch Process.

**568. Manufacture.**—

**a. Frasch method.** In the United States, the **Frasch method** is employed. In Texas and Louisiana there are deposits of sulfur several hundred feet below clay, rock, and quicksand. Sulfur is extracted by a method worked out by an American chemist, Hermann Frasch (Fig. 179).

A boring is made through the overlying material until the beds of sulfur are reached, and then through the opening three or four concentric pipes are driven. Superheated water (165° to 170°) is forced down the outside pipe or pipes, and it melts the sulfur, which runs into the sump at the foot of the well. Compressed hot air is forced to the bottom of the well through the smallest pipe, becoming mixed with the sulfur. The mixture of air and sulfur rises through the pipe surrounding the air-pipe, and sulfur is discharged into large vats constructed of boards.

*Courtesy of the Texas Gulf Sulphur Company*

FIG. 180. Sulfur bin.

The sulfur thus obtained is over 99.5 per cent pure, and the solidified product is used in commerce without further refining. A single well often produces 500 tons of sulfur daily, one well having been known to produce sulfur at the rate of 1,200 tons per day; and the most productive wells are said to have yielded more than 100,000 tons. A single block of the element has contained over 1,000,000 tons.

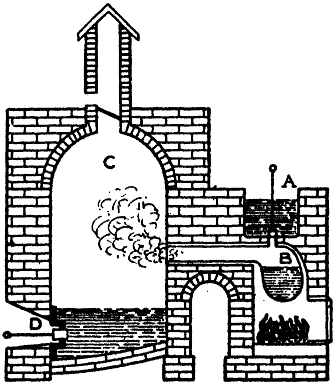


FIG. 181. Distillation of sulfur.

**b. Sicilian method.** In Sicily, sulfur is found mixed with earthy materials. The ore is heated in kilns; the sulfur melts and is collected in a pool near a tap-hole, from which it is drawn off from time to time.

Commercial Sicilian sulfur is refined by distillation from an iron retort (Fig. 181), the vapor passing into a large chamber, where it condenses, at the beginning, to **flowers of sulfur.** When the chamber becomes heated above the melting point of sulfur, it collects as a liquid which can be drawn off and then cast in slightly conical wooden moulds, and is called **roll sulfur.**

World production of sulfur was approximately 3,000,000 tons in 1938. Of this the United States produced 2,393,408 tons, Italy 374,339 tons, and Japan about 200,000 tons. Chile and Netherland East India produced about 20,000 tons each.

**569. Physical Properties.**—Like carbon and phosphorus, sulfur exists in several allotropic forms. These will be prepared with the materials listed in the following demonstration.

DEMONSTRATION 149. ALLOTROPIC FORMS OF SULFUR

Materials: (*a*) Flowers of sulfur, $CS_2$, clock-glass; (*b*) 100 cc. casserole half-full of flowers of sulfur over a burner; (*c*) 500 cc. casserole of roll sulfur heated nearly to boiling, 2-liter beaker of water (*d*) milk bottle containing ammonium polysulfide, concentrated HCl.

**a. Rhombic sulfur.** Sulfur occurs in nature as large yellow crystals belonging to the rhombic system. This form of sulfur may be obtained by allowing sulfur slowly to crystallize from solution in carbon disulfide. Rhombic sulfur has a specific gravity of 2.06, a melting point of 112.8°, and a boiling point of 444.6°; it is insoluble in water, but soluble in carbon disulfide. It is also called alpha-sulfur, written $S_\alpha$. It is the stable form of sulfur below 95.5°.

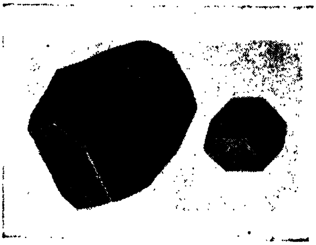


FIG. 182. Rhombic sulfur.

**b. Monoclinic sulfur.** Monoclinic sulfur (prismatic sulfur) may be prepared by heating rhombic sulfur until it just melts (no hotter), pouring it into a paper funnel, and, when the sulfur begins to solidify, quickly unfolding the paper. Long needles of sulfur will have formed. Fig. 183 shows these crystals formed by slow cooling in a casserole. The specific gravity of this form of sulfur is 1.96, and it melts at 118.9°; it is readily soluble in carbon disulfide. It is also called beta-sulfur, written $S_\beta$.

Rhombic and monoclinic sulfur are in equilibrium at 95.5°; above this temperature monoclinic sulfur is formed, whereas below this temperature rhombic sulfur is stable (Fig. 182). The crystals of monoclinic sulfur formed in the paper funnel gradually change into rhombic sulfur at room temperature.

**c. Amorphous sulfur.** When rhombic or monoclinic sulfur are heated, they melt at 112.8° and 118.9° respectively, forming the same pale-yellow liquid. At 159.9° the liquid suddenly turns dark-brown ($S_\lambda$) and becomes quite viscous. The maximum viscosity is reached at 230°, at which temperature it resembles tar ($S_\mu$). At higher temperatures it becomes less viscous, and at 444.6° it boils. These changes are illustrated in Fig. 184.

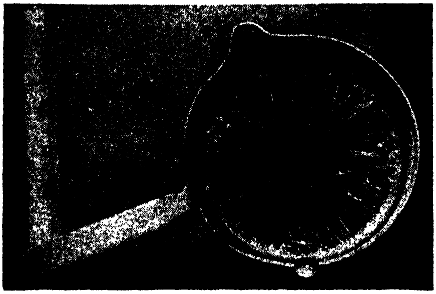
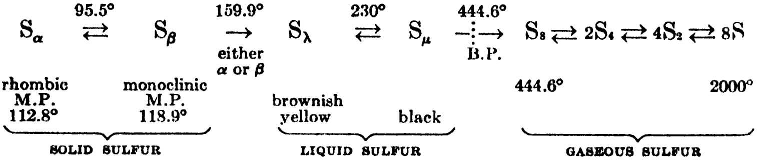


FIG. 183. Monoclinic sulfur, formed by slowly cooling molten sulfur.

If the more mobile liquid obtained at a higher temperature is suddenly chilled by pouring it in a thin stream into cold water, it will form a very viscous, transparent, elastic mass, known as **plastic sulfur** (Fig. 185). It is so viscous that it may be drawn out into long threads. Plastic sulfur is a supercooled liquid. The sulfur is cooled so rapidly that it does not have time to crystallize. On standing, however, it gradually changes to a hard brittle mass, which is in part rhombic sulfur. Solvents have but little action on plastic sulfur, but the crystalline part can be dissolved in $CS_2$.



95.5°
159.9°
230°
444.6°
$S_\alpha \rightleftarrows S_\beta \rightarrow S_\lambda \rightleftarrows S_\mu \rightarrow S_8 \rightleftarrows 2S_4 \rightleftarrows 4S_2 \rightleftarrows 8S$
either α or β
B.P.
rhombic M.P. 112.8°
monoclinic M.P. 118.9°
brownish yellow
black
444.6°
2000°
SOLID SULFUR
LIQUID SULFUR
GASEOUS SULFUR

FIG. 184. Sulfur Equilibria

**d. Milk of sulfur.** (*Lac sulfuris.*) When polysulfides are acidulated, tiny suspended particles of sulfur separate out, giving the appearance of milk, hence the term *milk of sulfur.* The particles are tiny crystals of rhombic sulfur. The equation is:

$$(NH_4)_2S_5 + 2HCl \rightarrow 2NH_4Cl + H_2S + 4S.$$

**Sulfur vapor** is octaatomic ($S_8$) at its boiling point. A series of equilibria exists between this temperature and 2000°. At this higher temperature and above, sulfur is monatomic (Fig. 184).

FIG. 185. Plastic sulfur, formed by pouring molten sulfur into water.

**570. Chemical Properties.**—Sulfur closely resembles oxygen in chemical properties. All the ordinary metals, except gold and platinum, unite with it to form sulfides, in some cases with the evolution of light. Silver tarnishes readily when in contact with sulfur; and when sulfur and mercury are rubbed in a mortar, mercuric sulfide ($HgS$) is formed.

Sulfur unites with most of the nonmetals. When heated in air it burns to form sulfur dioxide ($SO_2$); with hot carbon it forms carbon disulfide ($CS_2$); with chlorine, it forms liquid chlorides ($S_2Cl_2$,$SCl_2$,$SCl_4$); with hydrogen it forms hydrogen sulfide ($H_2S$).

When sulfur is treated with suitable oxidizing agents (*e.g.*, $HNO_3$) it is converted into sulfuric acid. Even the presence of moist air slowly brings this change about:

$$2H_2O + 3O_2 + 2S \rightarrow 2H_2SO_4.$$

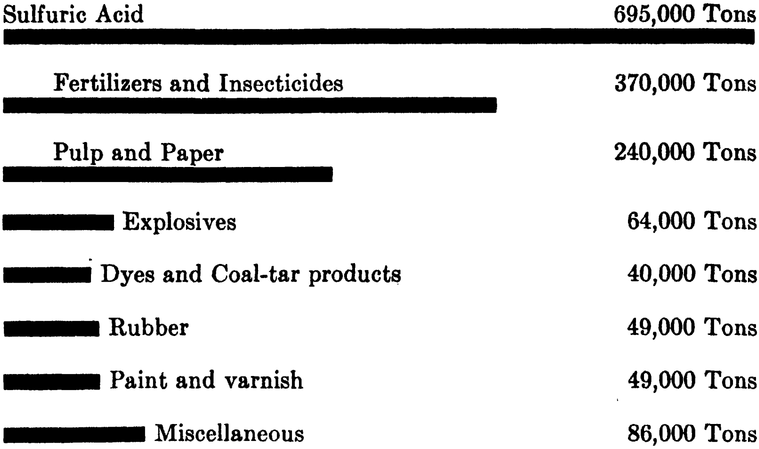
Sulfur probably forms more evil-smelling compounds than any other element. These are represented by hydrogen sulfide, associated with the analytical laboratory, and the sulfur compounds in onion and garlic.

**571. Uses.**—Sulfur is consumed chiefly in the manufacture of chemicals, in vineyards to destroy fungi, and in making bisulfite for the paper-pulp industry. In 1839 Charles Goodyear heated rubber with sulfur to 140°, and found that the product thereafter retained its elasticity in cold weather. This was the discovery of vulcanization which has made the present uses of rubber possible. Table 112 shows the consumption of sulfur in the United States in 1939.

## SELENIUM AND TELLURIUM

**572. Selenium.**—*Selenium* (Greek, meaning *the moon*) was discovered by Berzelius in 1817, who found it in the deposit from

TABLE 112. CONSUMPTION OF SULFUR (U. S. A., 1939, long tons)



sulfuric acid chambers. The element occurs in certain sulfides and in some specimens of native sulfur. Selenium is obtained as a by-product in the electrolytic refining of copper and lead.

Selenium, like sulfur, may be prepared in several allotropic modifications. The element is about as closely related to sulfur as bromine is to chlorine.

Selenium is used in two types of photocells. (*a*) *Photoelectric selenium cells* have the property of emitting electrons when light is shone upon the selenium surface. Photoelectric counters, automatic photoelectric controls on doors, etc., often employ the photoelectric selenium cell. Cells of Na, Cs, K, and copper oxides are also used. (*b*) *Photo-conductivity selenium cells* utilize the property of carefully annealed selenium to conduct electricity considerably better when light is shone upon it. Such cells have been in use many years; in 1914 Joel Stebbins constructed a delicate photometer of selenium for measuring the relative intensities of the light of the stars.

Selenium is used chiefly in the glass industry; a small quantity added to clear glass counteracts the greenish cast imparted by iron impurities. Ruby signal lenses contain 0.25 per cent Se. In 1939 there was 113 tons of selenium produced in the United States, and 62 tons was imported.

**573. Tellurium.**—This element was discovered by Müller von Reichenstein in 1782. The discovery was confirmed (1798) by

Klaproth, who named the element **tellurium** (Lat. *tellus*, the earth). The element occurs in small quantities in the free state, but it is generally found in combination with metals. Thus, *sylvanite* is a telluride of silver and gold $(AgAu)Te_2$. Tellurium is obtained as a by-product in the electrolytic refining of copper and lead, being extracted from the anode sludge. Tellurium does not resemble sulfur closely; it resembles antimony in appearance, being a silver-gray, metallic-looking substance. Its sp. gr. is about 6.26, and it is brittle. Tellurium is not of much commercial importance, but there is a small demand for use in radio tubes. Also, it is used to toughen rubber, and to harden lead. Domestic production of tellurium has been about 40 tons a year.

### HYDROGEN SULFIDE $H_2S$

**574. Occurrence and Preparation.**—Hydrogen sulfide occurs in certain volcanic gases and in the so-called sulfur waters, such as those of Harrogate. It is formed when various organic bodies (proteins) undergo putrefactive decomposition. Thus, the offensive smell of decomposing eggs is due in part to this gas. Many sulfides of metals, a source of hydrogen sulfide, are found in nature.

Hydrogen sulfide is best prepared by treating sulfides with dilute acids. For very pure gas, antimony trisulfide may be used; but for ordinary purposes ferrous sulfide is employed:

$$FeS + 2HCl \rightarrow FeCl_2 + H_2S \uparrow .$$

The preparation may be conveniently carried out in a Kipp apparatus. Dilute sulfuric acid may be substituted for HCl, but an oxidizing acid, such as $HNO_3$, cannot be used. The gas obtained with FeS is not pure since ferrous sulfide always contains more or less metallic iron.

**575. Physical Properties.**—Hydrogen sulfide is a colorless gas possessing a sweetish taste and a most offensive odor, similar to eggs long decomposed. The gas is a little heavier than air (sp.gr., 1.18). It may be readily condensed to a colorless liquid, the C.T. being 100.4° and the C.P. 89 atmos. The liquid boils at $-60°$. At 15°, 3.23 vols. of hydrogen sulfide are soluble in 1 vol. of water. The gas may be expelled completely by boiling its aqueous solution.

When hydrogen sulfide is inhaled, it acts as a powerful poison. One part of the gas in 200 parts of air is fatal to mammals; and small animals such as birds are more sensitive. Very dilute chlorine gas, obtained by sprinkling bleaching powder on a towel moistened with acetic acid, may be used as an antidote.

**576. Chemical Properties.**—Hydrogen sulfide is not a very stable compound, for it dissociates when heated:

$$H_2S \rightleftarrows H_2 + S.$$

This may be proved by holding a white porcelain dish in the flame of burning hydrogen sulfide. A yellow deposit of sulfur is obtained.

Hydrogen sulfide burns with a bluish flame:

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O.$$

Hydrogen sulfide tarnishes all of the elements in the electromotive force series from the most active down to, and including, silver. Silverware tarnishes from the action of hydrogen sulfide in the air.

**Hydrogen sulfide is a reducing agent.** For instance, a solution of ferric chloride is reduced to ferrous chloride by bubbling $H_2S$ through it, and potassium permanganate is decolorized:

$$2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S \downarrow,$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2S \\ \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S \downarrow.$$

**Hydrogen sulfide is a weak acid.** The relative quantities of ions present are as follows:

$$H_2S \rightleftarrows H^+ + SH^- \rightleftarrows {\scriptstyle 2H^+ + S^=}.$$

Actually, the hydrosulfide ion, $SH^-$, is less dissociated than is water, so that the concentration of sulfide ion, $S^=$, is exceedingly low. For this reason sodium sulfide, $Na_2S$, is strongly basic, hydrolyzing according to the scheme:

$${\scriptstyle S^= + HOH} \rightarrow SH^- + \underset{\text{basic}}{OH^-}.$$

**577. Hydrogen Sulfide in Qualitative Analysis.**—In analyzing a solution for cations, the scheme given in Table 113 is usually followed.

TABLE 113. ROUTINE QUALITATIVE ANALYSIS FOR METALS

<table>
<tr><td colspan="5">Solution containing all of the common cations, given below.<br>**Add 6N HCl in slight excess.**</td></tr>
<tr><td rowspan="4">Precipitate:<br>AgCl<br>$PbCl_2$<br>$Hg_2Cl_2$</td><td colspan="4">Solution: cations of groups 2–5.<br>**Make 0.3N with acid, and bubble in $H_2S$ gas.**</td></tr>
<tr><td rowspan="3">Precipitate:<br>HgS<br>PbS<br>$Bi_2S_3$<br>CdS<br>CuS<br>$SnS_2$<br>$Sb_2S_3$<br>$As_2S_3$</td><td colspan="3">Solution: cations of groups 3–5.<br>**Make basic with $NH_4OH$ and $(NH_4)_2S$ and bubble in more $H_2S$ gas.**</td></tr>
<tr><td rowspan="2">Precipitate:<br>$Al(OH)_3$<br>$Cr(OH)_3$<br>FeS<br>CoS<br>NiS<br>MnS<br>ZnS</td><td colspan="2">Solution: cations of groups 4–5. **Add $(NH_4)_2CO_3$.**</td></tr>
<tr><td>Precipitate:<br>$CaCO_3$<br>$BaCO_3$<br>$SrCO_3$<br>$(MgCO_3)$</td><td>In solution:<br>$Na^+$<br>$K^+$<br>$NH_4^+$</td></tr>
<tr><td>**GROUP 1**</td><td>**GROUP 2**</td><td>**GROUP 3**</td><td>**GROUP 4**</td><td>**GROUP 5**</td></tr>
</table>

Notice in Table 113 that groups 2 and 3 require the use of hydrogen sulfide gas. Group 2 represents those metals whose sulfides are *insoluble in dilute acids.* Group 3 represents those metals whose sulfides are soluble in dilute acids, but are *insoluble in basic solution.* Groups 4 and 5 include metals which are not precipitated by hydrogen sulfide in either solution. This important classification, based on the use of hydrogen sulfide gas, shows us why the chemist tolerates this disagreeable and extremely poisonous gas in the laboratory.

Following their separation into groups, the precipitates are further treated to identify the individual cations.

### DEMONSTRATION 150. FORMATION OF COLORED SULFIDES

Materials: Set-up in Fig. 186. The hydrogen sulfide comes from a Kipp generator.

The formation of sulfides is demonstrated in Fig. 186. Example:

$$\underset{\text{green}}{CuCl_2} + \underset{\text{gas}}{H_2S} \rightarrow \underset{\text{black}}{CuS} \downarrow + 2HCl.$$

Many of these sulfides are highly colored compounds: HgS, PbS, CuS, FeS, NiS, CoS (also $Ag_2S$ and $Hg_2S$) are black; $Bi_2S_3$ and $SnS_2$ are brown; CdS and $As_2S_3$ are yellow; $Sb_2S_3$ is orange; MnS is pale pink, and ZnS is white. $Al(OH)_3$ is colorless and gelatinous; $Cr(OH)_3$ is dark green and gelatinous.

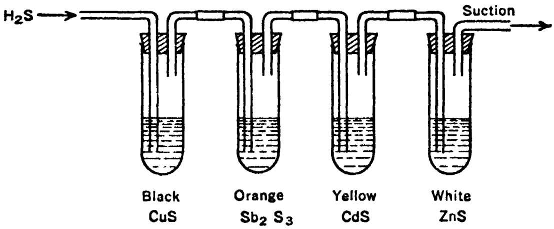


FIG. 186. Precipitation of sulfides in the qualitative analysis of metals (Dem. 150).

## QUESTION REVIEW

**General characteristics of the sulfur family (566).**

1. Predict chemical and physical properties for polonium.

I. SULFUR.

**a. History and occurrence (567). Manufacture (568).**

2. Give equations for the origin of native sulfur. What evidence substantiates this origin?
3. Describe the Frasch process. What percentage of world sulfur is produced by this method?

**b. Physical properties (569). Chemical properties (570).**

4. What equilibria exist (*a*) in sulfur gas; (*b*) in liquid sulfur; (*c*) in solid sulfur?
5. How would you make the following: milk of sulfur, $S_\lambda$, $S_\alpha$, $S_\mu$, $S_\beta$, plastic sulfur?
6. Show that sulfur resembles oxygen in its chemical properties.

**c. Uses (571).**

7. Calculate the percentages for each of the uses of sulfur in Table 112.

II. SELENIUM AND TELLURIUM (572–573).

8. State two interesting facts about these two elements.

III. HYDROGEN SULFIDE.

**a. Occurrence and preparation (574).**

9. What volume of 1N HCl is required to decompose 21.975 g. of ferrous sulfide?
10. If 250 cc. of HCl is required to decompose 10 g. of ferrous sulfide, what is the normality of the acid?

**b. Physical properties (575). Chemical properties (576).**

11. Compare and contrast the physical properties of $H_2S$ with those of $H_2O$.
12. Write equations showing (*a*) why $K_2S$ is strongly basic; (*b*) the tarnishing of silver; (*c*) $H_2S$ as a reducing agent.
13. Complete the following equations, indicating valence changes.

$$K_2Cr_2O_7 + H_2SO_4 + H_2S \rightarrow$$
$$HNO_3 + H_2S \rightarrow S + \cdots$$
$$H_2SO_4 + H_2S \rightarrow S + \cdots$$
$$SnCl_4 + H_2S \rightarrow$$

14. How may the following compounds be prepared: KSH, $K_2S$, PbS, FeS, and $(NH_4)_2S$?

**c. Hydrogen sulfide in qualitative analysis (577).**

15. Draw the scheme of routine qualitative analysis. Insert six sulfides and their colors.
16. Write the ionization of $H_2S$ in water. Is the $S^=$ concentration greater in acid or in alkaline media? Which, then, has the higher solubility product, CuS or FeS?
17. Account for the fact that substances such as CaS, $Al_2S_3$ and $Cr_2S_3$ cannot be prepared in the wet way, *i.e.*, in water solution.

**Reading References:** Articles number 47, 104, 201, 240, 241, 303, 315, 338 and 347 in the Appendix.

# CHAPTER XXXIX

## OXIDES AND OXY-ACIDS OF SULFUR

### SULFUR DIOXIDE AND SULFUROUS ACID

**578. Occurrence and Preparation.**—The ancients knew that when sulfur is burned, a gas with a sharp odor is formed. Fumes of burning sulfur were employed in fumigation. Priestley (1775) first prepared pure gaseous sulfur dioxide. Sulfur dioxide is evolved from active volcanoes, and it also occurs in very small quantities in the atmosphere over cities, where it is formed by the oxidation of sulfur in coal.

Sulfur dioxide is prepared in enormous quantities in the manufacture of sulfuric acid. The raw materials are either native sulfur, or iron pyrites ($FeS_2$), or the sulfide concentrates from zinc or copper ores. In all cases air is blown through the heated raw material:

$$S + O_2 \rightarrow SO_2,$$

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2.$$

Approximately 2,238,817 tons of native sulfur was produced in the United States in 1939; of this, 80 per cent came from Texas. The equivalent of approximately 5,000,000 tons of sulfur in pyrites was used in the rest of the world, of which Spain produces approximately 2,000,000 tons; Italy and Norway, 400,000 tons each; Germany, Portugal, the Island of Cyprus, and the United States, approximately 200,000 tons each. Also, nearly a million tons of sulfuric acid and 150,000 tons of sulfur are made as a by-product of copper and zinc smelters in the United States.

Sulfur dioxide in the laboratory is usually obtained from commercial tanks. It may be prepared likewise by (*a*) the interaction of concentrated sulfuric acid on copper turnings or (*b*) the treatment of a sulfite with an acid:

(*a*) $$Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O + SO_2 \uparrow,$$

(*b*) $$Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2 \uparrow.$$

The gas may be obtained by upward displacement of air; or a solution of it may be formed by bubbling the gas through water.

### DEMONSTRATION 151. FORMATION OF SULFUR DIOXIDE

Materials: Set-up in Fig. 187.

That $SO_2$, not $SO_3$, is the product of combustion of sulfur in oxygen may be demonstrated by the experiment illustrated in Fig. 187. No pressure change results from the combustion; if $SO_3$ had been formed, there would have been a decrease in pressure (why?).

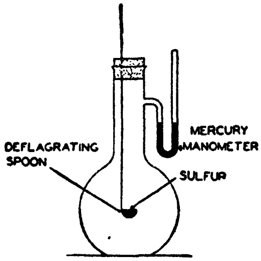


FIG. 187. $SO_2$ and not $SO_3$ is the product of burning sulfur in oxygen (Dem. 151).

**579. Physical Properties.**—Sulfur dioxide is a colorless gas possessing the sharp, suffocating odor associated with burning sulfur.

### DEMONSTRATION 152. PHYSICAL PROPERTIES OF SULFUR DIOXIDE

Materials: Tank of $SO_2$, with rubber and glass tubing, platinum dish over burner, ice and salt mixture in thermos bottle, 3 test-tubes, stoppered cylinder, 1-liter beaker; tongs.

Sulfur dioxide may be readily liquefied. The colorless liquid boils at −8°, and freezes to a white solid which melts at −76°. C.T. is 157°; C.P. 77.65 atmospheres. $SO_2$ is the freezing liquid used in domestic electric refrigerators (**518**). When the gas is passed into a test-tube surrounded by salt and ice, liquid $SO_2$ is formed. A dramatic experiment to demonstrate that it is cold is simultaneously to pour 2 cc. of liquid $SO_2$ and 2 cc. of water into a red-hot platinum dish. A lump of ice, reeking of $SO_2$ may be dumped out.

When a cylinder of $SO_2$ is immersed in a beaker of water, the gas dissolves, and the water rises into the cylinder. Eighty volumes of $SO_2$ dissolves in one volume of water at 0°.

**580. Chemical Properties and Uses.**—Sulfur has two principal positive valences, +4 and +6. The sulfur in $SO_2$ (valence +4) tends to react so as to increase to +6. That is, **sulfur dioxide is a reducing agent.** This is exemplified in the following reactions:

$$2SO_2 + O_2 \rightarrow 2SO_3,$$

$$SO_2 + Cl_2 \xrightarrow{\text{sunlight}} SO_2Cl_2 \text{ (sulphuryl chloride).}$$

$$2KMn^{+7}O_4 + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 2Mn^{+2}SO_4 + 2H_2SO_4.$$

### DEMONSTRATION 153. SULFUR DIOXIDE AS A REDUCING AGENT

Materials: Two glass cylinders of water, 2 glass cylinders of $SO_2$ gas; solutions of $KMnO_4$, $K_2Cr_2O_7$, and dilute $H_2SO_4$.

When acidified potassium permanganate solution is poured into $SO_2$ gas, the purple permanganate color disappears, since $Mn^{+7}$ is reduced to colorless $Mn^{+2}$ in accordance with the equation above. When acidified dichromate solution is poured into $SO_2$ gas, the orange $K_2Cr_2O_7$ solution becomes green, since the $SO_2$ reduces the $Cr^{+6}$ to $Cr^{+3}$, *i.e.*, green $Cr_2(SO_4)_3$.

### DEMONSTRATION 154. BLEACHING ACTION OF $SO_2$

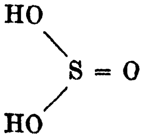
Materials: Red rose in bell-jar of oxygen; concentrated nitric acid; sulfur candle.

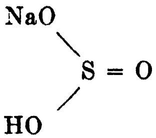
**Sulfur dioxide bleaches.** It is much milder in its action than chlorine, which would injure silks, woolens, etc. The bleaching action of sulfur dioxide may be shown by placing a lighted sulfur candle in a bell-jar containing a red rose. The rose turns to white. Color may be restored by dipping it in moderately strong nitric acid. In bleaching, water is necessary; and it is likely that sulfurous acid forms unstable compounds with the organic coloring matter. This is an important process for bleaching fruits such as marischino cherries, preparatory to dyeing them an attractive, uniform color. It also is a preservative. The law requires that a label warn the buyer that the fruit has been treated with $SO_2$.

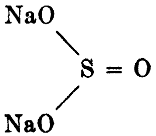
**581. Sulfurous Acid.**—Sulfurous acid is formed by dissolving sulfur dioxide in water. It ionizes as follows:

$$SO_2 + H_2O \rightleftarrows H_2SO_3 \rightleftarrows H^+ + HSO_3^- \rightleftarrows 2H^+ + SO_3^-.$$

Like $SO_2$, sulfurous acid is a good reducing agent, for it has a tendency to increase the valence of $S^{+4}$ to the valence $S^{+6}$. Salts of sulfurous acid are called **bisulfites and sulfites**, depending upon the number of atoms substituted for hydrogen:


sulfurous acid


sodium bisulfite


sodium sulfite

*Question*: What action will these substances have on litmus?

Sulfites combine with oxygen to form sulfates, ($SO_4^{=}$), and with sulfur to form thiosulfates ($S_2O_3^{=}$):

$$\begin{array}{lcl} 2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4, & & Na_2SO_3, O \\ & i.e. \langle & \\ Na_2SO_3 + S \rightarrow Na_2S_2O_3, & & Na_2SO_3, S \end{array}$$

### SULFUR TRIOXIDE AND SULFURIC ACID

**582. Sulfur Trioxide.**—Sulfur trioxide is formed by passing a mixture of oxygen and sulfur dioxide over a catalyst. Details of this reaction are given in the description of the contact process for manufacturing sulfuric acid. $SO_3$ can be formed also by heating certain bisulfates and sulfates, *e.g.*,

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3.$$

Sulfur trioxide is a colorless liquid which boils at 45°. It crystallizes at about 17°. A polymeric form may be obtained as white crystals resembling asbestos by allowing the liquid to stand in the presence of a trace of moisture. This form sublimes at 50°.

Sulfur trioxide fumes strongly in the air due to the formation of droplets of sulfuric acid. $SO_3$ reacts vigorously with water and interacts with metallic oxides to form sulfates:

$$H_2O + SO_3 \rightarrow H_2SO_4,$$
$$CaO + SO_3 \rightarrow CaSO_4.$$

**583. History.**—Sulfuric acid was obtained in the fifteenth century by heating green vitriol ($FeSO_4, 7H_2O$) with sand; hence the name "oil of vitriol," or "vitriolic acid." The acid thus prepared was very crude. About the middle of the eighteenth century Ward, a quack doctor of England, manufactured sulfuric acid by burning a mixture of sulfur and saltpeter in ladles suspended in glass globes containing small quantities of water. The capacity of the globes was from 40 to 50 gallons. The acid was crude and expensive, selling for 13 shillings ($3.25) per pound. Leaden chambers were soon substituted for the glass globes, which was a great step in advance. Such chambers were first constructed in Birmingham in 1746.

It is interesting to know that Squire and Messel in England and Winkler in Germany almost simultaneously (1875) took out patents for the manufacture of fuming sulfuric acid by "contact" processes. It was largely owing to the labors of Knietsch and Krauss (1901) that the commercial manufacture of sulfuric acid by the contact process was made a great success.

**584. Manufacture.**—Sulfuric acid is made by two important processes. The **contact process** for making concentrated acid such as is required in the dye industry, for which the process was developed, may be used only if the raw material contains no arsenic to poison the catalyst. The **lead chamber process** is used for the production of impure, dilute acid, such as might be suitable for the manufacture of fertilizers.

**585. The Contact Process.**—There are three stages in this process: (*a*) roasting sulfur or pyrites to form sulfur dioxide; (*b*) catalytic combination of the sulfur dioxide with oxygen to form sulfur trioxide; and (*c*) dissolving the sulfur trioxide in concentrated sulfuric acid to form fuming sulfuric acid, which is then diluted with water to the desired concentration.

(*a*) $S + O_2 \rightarrow SO_2$; $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$,
(*b*) $2SO_2 + O_2 \rightarrow 2SO_3$, + 45,000 cals.,
(*c*) $SO_3 + H_2SO_4 \rightarrow H_2SO_4{,}SO_3$ (fuming sulfuric acid),
$H_2SO_4{,}SO_3 + H_2O \rightarrow 2H_2SO_4$ (conc. sulfuric acid).

Also nearly a million tons of $H_2SO_4$ was made as a by-product of copper and zinc smelters in the United States.

(a) **As raw material** native sulfur, iron pyrites, or by-product sulfides from the zinc and copper smelters is used (tonnages are given in section **568**). The sulfur dioxide must be carefully freed of arsenic compounds which would poison the catalyst.

(b) **As catalyst** platinum, ferric oxide, or vanadium pentoxide is used. A porous magnesium sulfate coated with 0.25 per cent platinum has been found very efficient (Grillo catalyst); and at 450° yields of about 95 per cent $SO_3$ are obtained. Silica gel is also used as a support for the catalyst.

DEMONSTRATION 155. CONTACT PROCESS FOR $SO_3$

Materials: Set-up in Fig. 188.

(c) **The reaction** is demonstrated in Fig. 188.

If $O_2$ and $SO_2$ are passed over the cold catalyst, they emerge unaltered. A few seconds after a flame is placed under the catalyst mass, however, copious fumes of $SO_3$ are evolved, and may be liquefied in a tube surrounded by ice-water.

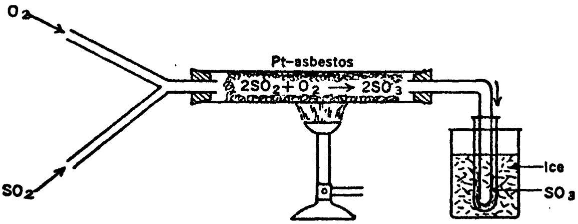
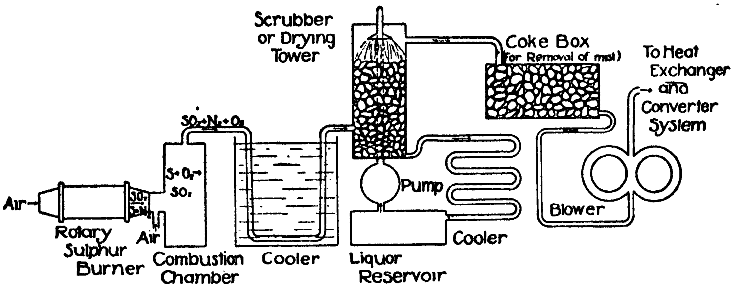


**Fig. 188.** Contact process for sulfur trioxide (Dem. 155).

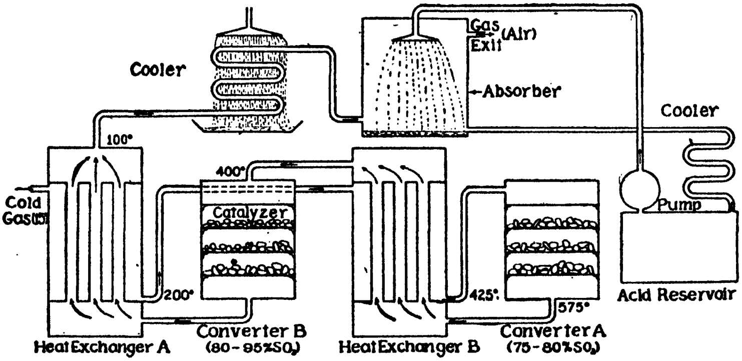
In industry, twice the quantity of oxygen demanded by theory is employed. Also, since the formation of $SO_3$ is exothermic, too high a temperature cannot be employed (why not?).

(d) **$SO_3$ dissolves** more readily in 97–99 per cent sulfuric acid than it does in water, so the $SO_3$ is passed into acid of this concentration. The concentration of the absorbing acid is kept constant by running in water as the trioxide is taken up. The contact process therefore produces fuming sulfuric acid; and accordingly it is used in preference to the lead chamber process (586) where (1) a concentrated acid is required, such as in the dye industry, and (2) the raw material (pyrites) contains little arsenic, etc., to poison the catalyst.



I Gas Preparation and Precipitation System

Contact Process for Sulphuric Acid



II. Heat Exchanger, Converter, and Absorption System

FIG. 189. Flow-sheet of the contact process for manufacturing oleum.

The details of the manufacture of fuming sulfuric acid or "oleum," a solution of $SO_3$ in $H_2SO_4$, are shown in Fig. 189.

Sulfur is burned in a Rotary Sulfur Burner, from which the gases pass to the Combustion Chamber to complete the combustion of sulfur to $SO_2$. After leaving the Cooler the gases pass through the Scrubber, or Drying Tower, where they are washed with sulfuric acid; thence through the Coke Box for the removal of mist. By means of a Blower the gases are next sent through Heat Exchangers *A* and *B* in order to raise the temperature to about 425°. They now enter Converter *A*, where, in the presence of the catalyst spread upon trays[1] (Grillo Process), the conversion of $SO_2$ to $SO_3$ is 75 to 80 per cent, the temperature rising to about 575°. The hot gases now pass through Heat Exchanger *B*, the temperature falling to about 400°. In passing through Converter *B* the percentage of $SO_3$ may rise to 95. The gases are now cooled down in preparation for the absorption of $SO_3$, by passing them through Heat Exchanger *A* and the Cooler. Finally, the gases are sent to the Absorber where the $SO_3$ is absorbed in concentrated sulfuric acid, forming "oleum." The residual gases ($N_2$, $O_2$, etc.) escape into the air and the acid collects in the Acid Reservoir.

**586. The Lead Chamber Process.**—In this process the catalyst is a gas, in contrast to the solid catalyst of the contact process. A diagram of the chamber process is given in Fig. 190.

**a. Production of $SO_2$** is accomplished in kilns (for $FeS_2$); or rotary burners (for native S):

$$S + O_2 \rightarrow SO_2.$$

**b. The Glover Tower.** At this stage $N_2O_3$, which is the catalyst, is added to the sulfur dioxide. (Actually a mixture of NO and $NO_2$ is used. For simplicity we shall write it $N_2O_3$.) These oxides come from the Gay-Lussac Tower (**d**).

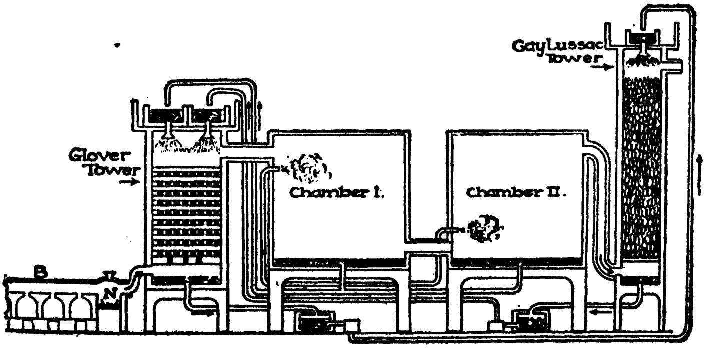


FIG. 190. The lead chamber process for manufacturing sulfuric acid.

**c. The Lead Chambers.** There are usually 3 to 5 chambers, with a total capacity of about 200,000 cubic feet. As a rule the greater part of the acid is formed in the first chamber, which is the largest. Here the gases react to form nitrosyl sulfuric acid in accordance with equation (1) below.

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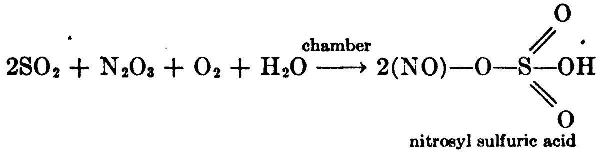
[1] Platinized asbestos is employed in tubular converters and not on trays.

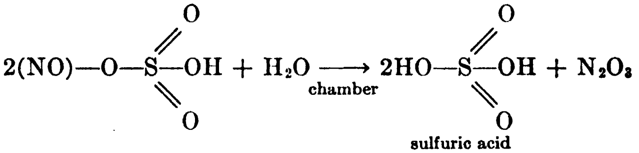
### DEMONSTRATION 156. FORMING NITROSYL SULFURIC ACID

Materials: Cylinder with its walls washed with 1 cc. of fuming nitric acid; $SO_2$ tank; $BaCl_2$.

When $SO_2$ is run into the cylinder, white crystals of nitrosyl sulfuric acid are coated on the cylinder. This dissolves in water to give $H_2SO_4$ (equation 2) which may be confirmed by adding $BaCl_2$ (?). In actual lead-chamber practice, however, these crystals do not form, since steam also is injected into the chamber, and immediately reacts with them:

(1) 

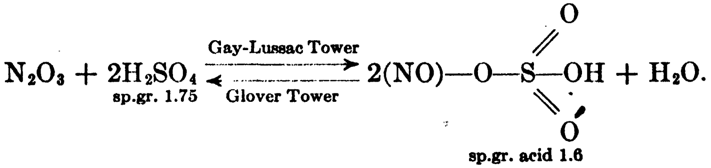
$$2SO_2 + N_2O_3 + O_2 + H_2O \xrightarrow{\text{chamber}} \underset{\text{nitrosyl sulfuric acid}}{2(NO)\text{—}O\text{—}\overset{\overset{O}{/\!/}}{\underset{\underset{O}{\backslash\backslash}}{S}}\text{—}OH}$$

(2) 

$$2(NO)\text{—}O\text{—}\overset{\overset{O}{/\!/}}{\underset{\underset{O}{\backslash\backslash}}{S}}\text{—}OH + H_2O \xrightarrow[\text{chamber}]{} \underset{\text{sulfuric acid}}{2HO\text{—}\overset{\overset{O}{/\!/}}{\underset{\underset{O}{\backslash\backslash}}{S}}\text{—}OH} + N_2O_3$$

The dilute sulfuric acid collects on the floors of the lead chambers, while the $N_2O_3$ passes into the Gay-Lussac Tower.

**d. The Gay-Lussac Tower.** The function of this tower is to recover the oxides of nitrogen. The process depends upon the following reversible reaction



$$N_2O_3 + \underset{\text{sp.gr. 1.75}}{2H_2SO_4} \xrightleftharpoons[\text{Glover Tower}]{\text{Gay-Lussac Tower}} \underset{\text{sp.gr. acid 1.6}}{2(NO)\text{—}O\text{—}\overset{\overset{O}{/\!/}}{\underset{\underset{O}{\backslash\backslash}}{S}}\text{—}OH} + H_2O.$$

In the Gay-Lussac tower the rising gases of $N_2O_3$ meet and dissolve in $H_2SO_4$ sp. gr. 1.75 which is sprayed from above, and trickles down over tile. The solution is then pumped around to the Glover Tower. Here acid is diluted to sp. gr. 1.6, thereby reversing the reaction, and releasing the $N_2O_3$ to a new batch of $SO_2$. As the lower part of the Glover Tower is hot, the water evaporates and the acid increases in sp. gr. to 1.75, so that it may be used again in the Gay-Lussac Tower.

Unlike the acid produced in the contact process, the lead-chamber acid contains impurities, such as lead sulfate and arsenic compounds. Also, it is only 60–70 per cent $H_2SO_4$, and must be further concentrated. This may be done either (*a*) by diluting with "oleum" made by the contact process or (*b*) by evaporating in lead pans to sp. gr. 1.70 (more concentrated acid would attack the lead pan), followed by evaporating as it trickles down a heated, inclined flue.

**587. Physical Properties.**—Sulfuric acid obtained by distillation is a heavy, oily liquid sometimes called "oil of vitriol." If the distillate containing about 98 per cent of $H_2SO_4$ is cooled considerably below 0°, white crystals of hydrogen sulfate are formed, which melt at 10.5°. The sp.gr. of the liquid at 15° is 1.837. When the pure acid is heated, it fumes by reason of partial dissociation into water and sulfur trioxide. The latter escapes until the acid contains 98.33 per cent of $H_2SO_4$. The liquid then boils constantly at 338° without change in concentration. Sulfuric acid dissolves in water with considerable evolution of heat, and dangerous spattering occurs if water is added to it. The rule to follow is:

> "The water should be in before
> You add the $H_2SO_4$."

**588. Chemical Properties.**—Concentrated sulfuric acid is entirely different from dilute sulfuric acid in its behavior.

*a.* Concentrated acid **is unstable.** Heated above 100°, concentrated sulfuric acid dissociates into water and sulfur trioxide; and at 450° the dissociation is complete:

$$H_2SO_4 \rightarrow H_2O + SO_3.$$

*b.* Concentrated sulfuric acid is **an oxidizing agent.** When concentrated sulfuric acid reacts with metals, sulfur dioxide is formed. Hydrogen is not evolved unless the acid is dilute.

$$Cu + 2H_2SO_{4\,\text{conc.}} \rightarrow CuSO_4 + 2H_2O + SO_2 \uparrow .$$

Platinum and gold are appreciably attacked.

*c.* Concentrated sulfuric acid has a great **affinity for water.**

DEMONSTRATION 157. AFFINITY OF $H_2SO_{4\text{conc.}}$ FOR WATER

**Materials:** Concentrated sulfuric acid; paper, lump of sugar, wood splint; 100 cc. of concentrated sulfuric acid, 120 g. sucrose dissolved in 100 cc. water, 400 cc. beaker set on a cardboard box.

Concentrated sulfuric acid abstracts the elements of water from many organic compounds, such as sugar ($C_{12}H_{22}O_{11}$) and starch $(C_6H_{10}O_5)_x$. This may be shown very impressively by pouring the acid into a very concentrated solution of cane sugar. Much heat is evolved, the sugar being converted largely into carbon and water:

$$C_{12}H_{22}O_{11} \rightarrow 12C + 11H_2O.$$

Wood, paper, and cotton are also charred by sulfuric acid. White cards written upon with dilute sulfuric acid appear blank; but upon heating them, the acid becomes concentrated and chars the paper and the writing starts into view.

*d.* Sulfuric acid **decomposes salts** of other acids having boiling points lower than that of sulfuric acid. The preparation of hydrochloric acid (143) is a typical example. On account of its high boiling point, stability, and cheapness, sulfuric acid is the most important acid used in the preparation of other acids.

*e.* **Dilute sulfuric acid** has properties quite different from those for concentrated acid, for in dilute aqueous solution the reactions are ionic, while in that of concentrated sulfuric acid they are molecular. Sulfuric acid is an active acid.

$$H_2SO_4 \rightleftarrows H^+ + HSO_4^- \underset{\text{increases with dilution}}{\rightleftarrows 2H^+ + SO_4^=}.$$

**589. Sulfates and Bisulfates.**—Salts of sulfuric acid contain the $SO_4^=$ or $HSO_4^-$ ions, and are called sulfates and bisulfates respectively, *e.g.*, sodium sulfate, $Na_2SO_4$, and sodium bisulfate, $NaHSO_4$.

Certain sulfates are known as **vitriols:**

| | |
|---|---|
| Blue vitriol | $CuSO_4, 5H_2O$ |
| Green vitriol | $FeSO_4, 7H_2O$ |
| White vitriol | $ZnSO_4, 7H_2O$ |

*Epsom salt,* $MgSO_4, 7H_2O$; *gypsum,* $CaSO_4, 2H_2O$; and *potash alum,* $K_2SO_4, Al_2(SO_4)_3, 24H_2O$, are other important sulfates.

The presence of the **sulfate ion is detected** by the addition of an acid solution of barium chloride; this forms a white precipitate:

$$Ba^{++} + SO_4^= \rightarrow \underset{\text{white}}{BaSO_4} \downarrow .$$

**590. Uses.**—Sulfuric acid is the most important and useful acid known. Next to water, it is the fluid most widely employed in the chemical industries. The acid plays such an important part that it has appropriately been called the "yardstick of civilization." A country's prosperity may be estimated roughly from its output of sulfuric acid.

Immense quantities of the acid are combined with ammonia to form one of the most important fertilizers, ammonium sulfate. Sulfuric acid is employed extensively in petroleum refining, and as a catalyst in the petroleum industry, in rayon and pyroxylin manufacture, in metallurgy and in the manufacture of steel, and in the paint and pigment industry. Deprived of this acid, we could not operate our lead storage batteries, manufacture explosives, or transform insoluble phosphate rock or bone-ash into soluble acid phosphate, so necessary in agriculture. It is truly "the vital fluid of the nation's industries."

Consumption of sulfuric acid (as 63 per cent $H_2SO_4$) in short tons in the United States for 1939 is given in Table 114.

TABLE 114. SULFURIC ACID CONSUMPTION BY INDUSTRIES

| | |
|---|---|
| Fertilizer | 2,100,000 |
| Petroleum | 1,210,000 |
| Iron and Steel | 980,000 |
| Chemicals | 975,000 |
| Coal-tars | 740,000 |
| Metallurgy (not steel) | 570,000 |
| Paints | 500,000 |
| Rayon | 400,000 |
| Miscellaneous | 706,000 |
| TOTAL............ | 8,181,000 |

OXIDES AND OXY-ACIDS OF SULFUR

TABLE 115. OXIDES AND OXY-ACIDS OF SULFUR

| oxides | | ous-acids | | ic-acids | |
|---|---|---|---|---|---|
| monoxide | $SO$ | Sulfurous acid | $H_2SO_3$ | Sulfuric | $H_2SO_4$ |
| dioxide | $SO_2$ | Hyposulfurous acid | $H_2S_2O_4$ | Thiosulfuric | $H_2S_2O_3$ |
| trioxide | $SO_3$ | | | Caro's | $H_2S_2O_5$ |
| heptoxide | $S_2O_7$ | | | Pyrosulfuric | $H_2S_2O_7$ |
| | | | | Persulfuric | $H_2S_2O_8$ |

Also: dithionic acid, trithionic acid, etc., $H_2S_aO_6$ where $a = 2, 3, 4, 5, 6$.

**591. Thiosulfuric Acid.**—*Thiosulfuric acid,* $H_2S_2O_3$, is unknown in the free state. **Sodium thiosulfate,** its most important salt, may be prepared by boiling a solution of sodium sulfite with sulfur:

$$Na_2SO_3 + S \rightarrow Na_2S_2O_3.$$

This action is similar to the addition of oxygen to sulfurous acid. The hydrate, $Na_2S_2O_3, 5H_2O$, is commonly known as "**hypo,**" and its solution is used in photography in the fixing bath as a solvent for silver salts.

When a solution of sodium thiosulfate is treated with an acid, sulfur and sulfur dioxide are set free:

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + H_2S_2O_3 \rightarrow S \downarrow + H_2SO_3 \rightleftarrows H_2O + SO_2 \uparrow.$$

The sulfur which is deposited is yellow.

An iodine solution is decolorized by a solution of a thiosulfate:

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + \underset{\text{Sodium tetrathionate}}{Na_2S_4O_6}.$$

**592. Pyrosulfuric Acid.**—Sulfur trioxide and sulfuric acid interact to form pyrosulfuric acid, $H_2S_2O_7$. This is a solid compound. "**Oleum**" is sulfuric acid containing about 20 per cent of pyrosulfuric acid; it is used extensively in chemical industries. The acid fumes when exposed to air. The old "Nordhausen" or "fuming" sulfuric acid contained from 10 to 20 per cent extra of $SO_3$. The salts of pyrosulfuric acid are called **pyrosulfates;** they may be obtained by heating acid sulfates:

$$2NaHSO_4 \rightleftarrows Na_2S_2O_7 + H_2O.$$

The bisulfates of sodium and potassium are often employed as **fluxes.** For instance, in analytical operations silica ($SiO_2$) may be separated from alumina ($Al_2O_3$) and ferric oxide ($Fe_2O_3$) by fusing the mixture in a platinum crucible with the bisulfate. Silica is not attacked, but alumina and ferric oxide are transformed into soluble sulfates. It is of interest to note, also, that alumina and ferric oxide can be separated from silica by adding hydrofluoric acid and then evaporating to dryness; $SiO_2$ is transformed into $SiF_4$, which is gaseous (469).

**593. Persulfuric Acid.**—This acid, which has the formula $H_2S_2O_8$, can be formed at the anode by the electrolysis of fairly concentrated sulfuric acid in which the ion $HSO_4^-$ predominates:

$$2HSO_4^- \rightarrow H_2S_2O_8 + 2e.$$

The anhydride of persulfuric acid is $S_2O_7$, a liquid:

$$H_2O + S_2O_7 \rightleftarrows H_2S_2O_8.$$

**Sulfur heptoxide** may be obtained by subjecting a mixture of dry sulfur trioxide and oxygen to the silent electric discharge.

**Persulfates,** or the salts of persulfuric acid, are powerful oxidizing agents, and find application as such. Ammonium persulfate, a white crystalline compound, may be prepared by electrolysis, a saturated solution of ammonium sulfate being employed at the anode and fairly strong sulfuric acid at the cathode. The salt is collected in a porous pot. In a similar manner, potassium persulfate is produced by electrolysis, a solution of $KHSO_4$ being employed at the anode. *The persulfates are soluble in water, and are gradually decomposed by it, oxygen being formed:*

$$2H_2S_2O_8 + 2H_2O \rightarrow 4H_2SO_4 + O_2,$$
$$2K_2S_2O_8 + 2H_2O \rightarrow 4KHSO_4 + O_2.$$

**594. Other Oxyacids of Sulfur.**—**Sodium hyposulfite,** a salt of hyposulfurous acid ($H_2S_2O_4$), is used by the calico printer and dyer as a reducing agent for indigo. A solution of the salt may be obtained by the interaction of zinc, sodium bisulfite, and sulfurous acid:

$$Zn + 2NaHSO_3 + H_2SO_3 \rightarrow Na_2S_2O_4 + ZnSO_3 + 2H_2O.$$

Indigo, an insoluble compound, is reduced by sodium hyposulfite to indigo-white, which is soluble. When cloth is treated with the mixture, and then exposed to the air, oxygen is taken up and indigo re-formed.

The **polythionic acids** (di-, tri-, tetra-, penta-, and hexathionic acids) are not of great importance. They may be formed, along with free sulfur, by passing $SO_2$ and $H_2S$ alternately into *water:*

$$H_2S + 3SO_2 \rightarrow H_2S_4O_6,$$
$$2H_2S + 6SO_2 \rightarrow H_2S_3O_6 + H_2S_5O_6.$$

We have seen that sodium tetrathionate ($Na_2S_4O_6$) is formed when sodium thiosulfate is treated with iodine (591). (What change occurs when the *gases* $SO_2$ and $H_2S$ interact?)

## QUESTION REVIEW

### I. SULFUR DIOXIDE AND SULFUROUS ACID.

**a. Occurrence and preparation** (578).

1. Give equations showing the preparation of sulfur dioxide from (*a*) zinc blende; (*b*) the chief industrial source.

**b. Physical properties** (579). **Chemical properties** (580).

2. How much water is required to dissolve 40 g. of $SO_2$ at 0°?
3. What is the weight of 1 liter of $SO_2$ at S.T.P. (at. wts. $S = 32, O = 16$)?
4. Complete the following equations:
   (*a*) $H_2O_2 + H_2SO_3 \rightarrow$
   (*b*) $Cl_2 + H_2O + H_2SO_3 \rightarrow$
   (*c*) $FeCl_3 + H_2O + H_2SO_3 \rightarrow$
   (*d*) $K_2Cr_2O_7 + H_2SO_3 + H_2SO_4 \rightarrow$

**c. Sulfurous acid** (581).

5. Indicate how sulfurous acid ionizes. Utilize this in explaining the action of $KHSO_3$ and of $K_2SO_3$ solutions on litmus paper.

### II. SULFUR TRIOXIDE AND SULFURIC ACID.

**a. Sulfur trioxide** (582).

6. Draw up a table contrasting the physical properties of $SO_2$ with those of $SO_3$.

**b. History** (583) **and manufacture** (584–586) **of sulfuric acid.**

7. How old are the two processes for manufacturing $H_2SO_4$?
8. Contrast the products obtained in the two processes.
9. Give equations for (*a*) the contact process; (*b*) the lead chamber process. Underline the catalysts.
10. What is the function of the (*a*) Rotary Sulfur Burner, (*b*) Glover Tower, (*c*) Gay-Lussac Tower, (*d*) Lead Chamber, (3) Grillo catalyst mass?

**c. Physical properties** (587). **Chemical properties** (588).

11. What precautions should be taken in mixing $H_2O$ and $H_2SO_4$?
12. State three chemical properties in which concentrated sulfuric acid differs from dilute sulfuric acid. Give equations for each one.
13. Show the electron transfers in the reaction between concentrated sulfuric acid and (*a*) copper, (*b*) mercury.

**d. Sulfates and bisulfates** (589).

14. Identify: blue vitriol, bisulfite ion, bisulfate ion, Epsom salt, an insoluble white sulfate.

**e. Uses for sulfuric acid** (590).

15. Draw a chart similar to that in Table 114 showing the percentages of sulfuric acid consumed in various industries.

III. OXIDES AND OXY-ACIDS OF SULFUR (591–594).

16. If 40 cc. of 1M $Na_2S_2O_3$ is required to decolorize 25 cc. of a solution of iodine, what is its normality?
17. Identify, and give one important fact about each of the following: $Na_2S_2O_3$; $NaHSO_4$; $Na_2S_2O_7$; $Na_2S_4O_6$; $H_2S_2O_4$, $H_2S_3O_6$, $K_2S_2O_8$, $H_2S_2O_8$.

**Reading References:** Articles number 133, 338 and 347 in the Appendix. See, also, articles on sulfur: 47, 104, 201, 240, 241 and 315.

# CHAPTER XL

## THE HALOGEN FAMILY. GROUP VII-B

**595. General Characteristics of Group VII-B.**—The elements in Group VII-B are known as **the halogen family** (Greek, *salt-producers*) and include **fluorine, chlorine, bromine, iodine** and **element No. 85.**

**a. Occurrence.** The four lightest halogens occur very widely distributed in nature as binary salts, called **halides.** These include NaCl, KCl, $MgBr_2$, and $CaF_2$ (Table 116).

TABLE 116. ABUNDANCE OF THE HALOGENS

| HALOGEN | % IN EARTH'S CRUST | IN SEA-WATER PARTS PER MILLION |
|---|---|---|
| Fluorine | 0.1 | negligible |
| Chlorine | 0.1 | 10,000 |
| Bromine | 0.001 | 67 |
| Iodine | 0.0001 | 7 |

Fluorine, it will be noticed, is relatively abundant in the earth's crust, but is practically absent from sea-water; this means that fluorides are not very soluble, and so are not carried down into the sea. Element No. 85 has not been isolated; although an artificial radioactive isotope of it was produced in the cyclotron in 1940.

**b. Preparation of Free Halogens.** The free halogens may be prepared (1) by electrolysis, under proper conditions, of a halide; (2) by treating HCl, HBr and HI with an oxidizing agent such as $MnO_2$; (3) by displacement (**136, b**). Equations representing these methods follow.

(1) $$2NaCl \xrightarrow[\text{of molten NaCl}]{\text{electrolysis}} 2Na + Cl_2,$$

(2) $$(O) + 2HCl \rightarrow H_2O + Cl_2,$$

(3) $$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2.$$

**c. Physical Properties of the Halogens.** Some properties of the halogens are given in Table 117.

It is noticed from the table that there is a gradual change in passing from the lightest to the heaviest member of the family.

TABLE 117. THE HALOGEN FAMILY

| | FLUORINE, F | CHLORINE, Cl | BROMINE, Br | IODINE, I |
|---|---|---|---|---|
| At. wt. | 19.00 | 35.457 | 79.916 | 126.92 |
| At. no. | 9 | 17 | 35 | 53 |
| Planetary arrangement | 2-7 | 2-8-7 | 2-8-18-7 | 2-8-18-18-7 |
| B.P. | −187° | −34.6° | 58.5° | 183° |
| M.P. | −223° | −101.6° | 7.2° | 113.5° |
| Density | 1.14 (liq.) | 1.87 (liq.) | 3.12 (liq.) | 4.95 (solid) |
| Color | Pale yellow | Greenish yellow | Red-brown | Dark grey |
| Usual state | gas | low gas | liquid | solid |
| Hydrides | $H_6F_6$ | HCl | HBr | HI |

Oxides and Oxy-compounds: see Table 118, section 614.

The color deepens, ranging from pale yellow fluorine to steel-grey iodine. The boiling points, melting points and densities gradually increase; and for chlorine and bromine are very roughly the average of the elements immediately following and preceding in the table (*e.g.*, B.P. of Br = 58.5° whereas the average for Cl and I is $\frac{1}{2}(-34.6 + 183) = 74.2°$). This was one of Döberiner's famous *triads* (281).

**d. Chemical Properties of the Halogens.** The halogens are the most non-metallic elements known, their electronegativity increasing with decreasing atomic weight (*e.g.*, fluorine is the most active non-metal known).

DEMONSTRATION 158. RELATIVE REACTIVITY OF THE HALOGENS

Materials: 50 cm. × 20 mm. tubing, clamped horizontally; inside, near one end, place a 5 cm. × 18 mm. tubing of KI, and near the other end, a 5 cm. × 18 mm. tubing of KBr. Connect a flask of $Cl_2$ to the KBr end, and a water aspirator to the KI end. Burner under the KI end.

Demonstration 158 shows the relative reactivity of the halogens. Yellow chlorine gas passing over KBr liberates reddish-brown $Br_2$; this, in turn, passing over KI liberates violet $I_2$ vapor; so that all three halogens are simultaneously visible in the different portions of the apparatus:

$$Cl_2 + 2KBr \rightarrow 2KCl + Br_2 \uparrow.$$
$$Br_2 + 2KI \rightarrow 2KBr + I_2 \uparrow.$$
$$Cl_2 + 2KI \rightarrow 2KCl + I_2 \uparrow \text{ also occurs.}$$

### DEMONSTRATION 159. COMBINATION OF HALOGENS WITH METALS

**Materials:** Three large tubes (Dumas tubes) containing $Cl_2$, $Br_2$, and $I_2$ respectively, the latter two over burners; antimony powder in salt shaker.

The halogens unite directly with most metals to form halides, the reaction with chlorine being more vigorous than that of iodine:

$$2Sb + 3Cl_2 \rightarrow 2SbCl_3,$$
$$\text{"} \quad 3Br_2 \rightarrow 2SbBr_3,$$
$$\text{"} \quad 3I_2 \rightarrow 2SbI_3.$$

Fluorine does not unite directly with gold or platinum, which are attacked by chlorine. Iodine forms the most stable oxides,—$I_2O_4$ and $I_2O_5$. It is an extraordinary fact that the extremely electronegative fluorine atoms unite to form molecules ($F_2$), yet they are unable to combine directly with oxygen which approaches fluorine in electronegative character.

The halogens possess a multiple valence which varies from $-1$ to $+7$, as is illustrated in Table 118, section **614**.

**e. The Halogen Acids.**—All of the halogens unite with hydrogen to form halogen acids:

$$H_2 + I_2 \rightleftarrows 2HI.$$

They may also be prepared by **hydrolysis** (Greek, *water + to loosen*) of halides of phosphorus and of other non-metals:

$$PBr_3 + 3HOH \rightarrow 3HBr + H_3PO_3,$$
$$PI_3 + 3HOH \rightarrow 3HI + H_3PO_3.$$

Hydrochloric acid is prepared by the action of concentrated sulfuric acid upon a halide:

$$H_2SO_4 + NaCl \rightarrow NaHSO_4 + HCl \uparrow,$$

but pure HBr or HI cannot be prepared by this method since they react further with the sulfuric acid:

$$2HBr + H_2SO_4 \rightarrow 2H_2O + SO_2 \uparrow + Br_2 \uparrow,$$
$$8HI + H_2SO_4 \rightarrow 4H_2O + H_2S \uparrow + 4I_2 \uparrow.$$

All of the halogen acids are colorless gases (B.P. HF, +19.4°; HCl, −85°; HBr, −67°; HI, −36°). They are very soluble in water. HF is the most stable and HI the least stable of the halogen acids.

**f. Halogen Oxy-acids.**—As is shown in Table 118, the halogens form **oxy-acids** of similar character, such as

| | |
|---|---|
| Hypochlorous acid | $HClO$ |
| Chlorous acid | $HClO_2$ |
| Chloric acid | $HClO_3$ |
| Perchloric acid | $HClO_4$ |

These compounds are taken up in detail in sections **615–619.**

In general, the stability of the oxygen compounds of the halogens increases from chlorine to iodine. Thus, iodine is able to displace chlorine from chloric acid or chlorates:

$$2HClO_3 + I_2 \rightarrow 2HIO_3 + Cl_2.$$

### FLUORINE $^{19.00}_{9}F$

**596. History and Occurrence.**—The brilliant French chemist Moissan (1886) achieved the difficult task of preparing fluorine.

Long before Moissan succeeded in liberating fluorine, it was known that fluorspar contained calcium in combination with an element analogous to chlorine. The element was named "fluorine," owing to the use of fluorspar as a flux (Latin *fluo*, I flow) in metallurgy.

**Fluorspar**, $CaF_2$, is the most common mineral containing fluorine. Fluorine occurs in large quantities in the mineral **cryolite**, $3NaF, AlF_3$, which is found in Greenland. Fluorine also occurs in a large number of other minerals, and in very small quantities in certain mineral waters. It also is found in bones of animals and in teeth, and traces have been detected in the blood, milk, and brains of animals.

**597. Preparation.**—Fluorine may be prepared by electrolysis of molten potassium hydrogen fluoride ($KHF_2$) in copper vessels, using graphite electrodes. Hydrogen is evolved at the cathode; and fluorine gas, at the anode.

Moissan first prepared it by electrolysis at −23° using liquid hydrogen fluoride containing potassium hydrogen fluoride to make it a conductor.

**598. Properties of Fluorine.**—Fluorine is a pale greenish-yellow gas about 1.3 times as heavy as air. It may be condensed to a pale-yellow liquid, which boils at −187°.

In its chemical action fluorine is very similar to chlorine, but much more active. In fact, fluorine is the most active element known. Thus many elements, such as sulfur, phosphorus, carbon, silicon, and boron, catch fire in fluorine. Most metals also burn in fluorine, but gold and platinum are but slightly attacked below a red heat. Fluorine displaces chlorine, bromine, and iodine from their halides; also fluorine displaces oxygen from water, converting it into ozone:

$$3F_2 + 3H_2O \rightarrow 3H_2F_2 + O_3.$$

**599. Hydrogen Fluoride.**—Hydrogen and fluorine combine instantly, even at the melting point of hydrogen (−259°), at which temperature fluorine is a solid.

**a. Preparation.**—Hydrogen fluoride, or hydrofluoric acid, is best prepared by heating fluorspar, $CaF_2$, with concentrated sulfuric acid in a platinum or lead vessel; or by heating potassium hydrogen fluoride:

$$(1) \qquad CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF \uparrow,$$

$$(2) \qquad KHF_2 \rightarrow KF + HF \uparrow.$$

The vapor may be condensed to a liquid, or absorbed in water, the solution being known as hydrofluoric acid. The acid is sold in bottles made of ceresin wax or gutta-percha.

**b. Properties.**—Hydrogen fluoride is a colorless liquid, boiling at 19.54° and solidifying at −102.5°. It is very soluble in water. Pure hydrogen fluoride is a non-conductor of electricity.

The weight of 22.4 liters of HF vapor at 90° is 20; this corresponds to the formula HF (1.008 + 19.00). At lower temperatures the density of the vapor is greater, indicating that HF is polymerized. Actually, an equilibrium exists between the monomer HF and the polymer $H_6F_6$, that is, $6HF \rightleftarrows H_6F_6$, and at its boiling point (19°) approximately 80 per cent of the hydrogen fluoride is present as the polymer $H_6F_6$.

**c. Chemical reactions.**—Hydrogen fluoride is extremely poisonous. Nicklés of Nancy died, in 1869, from accidentally breathing HF vapor while trying to prepare fluorine.

The most important reaction of HF is its etching of glass (review section **469**), during which the gaseous substance silicon tetrafluoride, $SiF_4$, is formed:

$$\underset{\text{soda-glass}}{Na_2SiO_3} + 6HF \rightarrow 2NaF + 3H_2O + \underset{\substack{\text{silicon}\\ \text{tetrafluoride}}}{SiF_4} \uparrow.$$

The etching may be accomplished either with the vapor or the aqueous solution. In the first instance a rough surface is obtained; in the latter, a smooth etching.

**d. Fluorides.**—Calcium fluoride, **fluorspar,** or **fluorite,** $CaF_2$, is the most important salt of hydrofluoric acid.

415,000 metric tons of this important mineral was produced in 1938, of which Germany produced 161,341 tons, and the United States 72,940 tons; U. S. S. R. has also become an important producer.

Fluorspar is consumed chiefly as a flux in the metallurgical industry. 116,200 tons was consumed in the United States in the Basic Open-hearth; 26,000 tons, in the manufacture of hydrofluoric acid; and 21,400 tons, in white enamels and glass.

**Cryolite,** $AlF_3, 3NaF$, a double fluoride of aluminum and sodium, is used in the aluminum industry (377), although a synthetic calcium-sodium fluoride is often substituted for it. World production in 1939 was 10,210 long tons of cryolite; of this 9,300 tons came from Ivigtut, Greenland.

## CHLORINE $^{35.457}_{17}Cl$

**600. Chlorine Chemistry.**—The chemistry of chlorine has been treated in Chapters XII and XIII.

## BROMINE $^{79.92}_{35}Br$

**601. History and Occurrence.**—Bromine was discovered by the French chemist Balard in the year 1826; he named the element **bromine** (Greek, *a stench*).

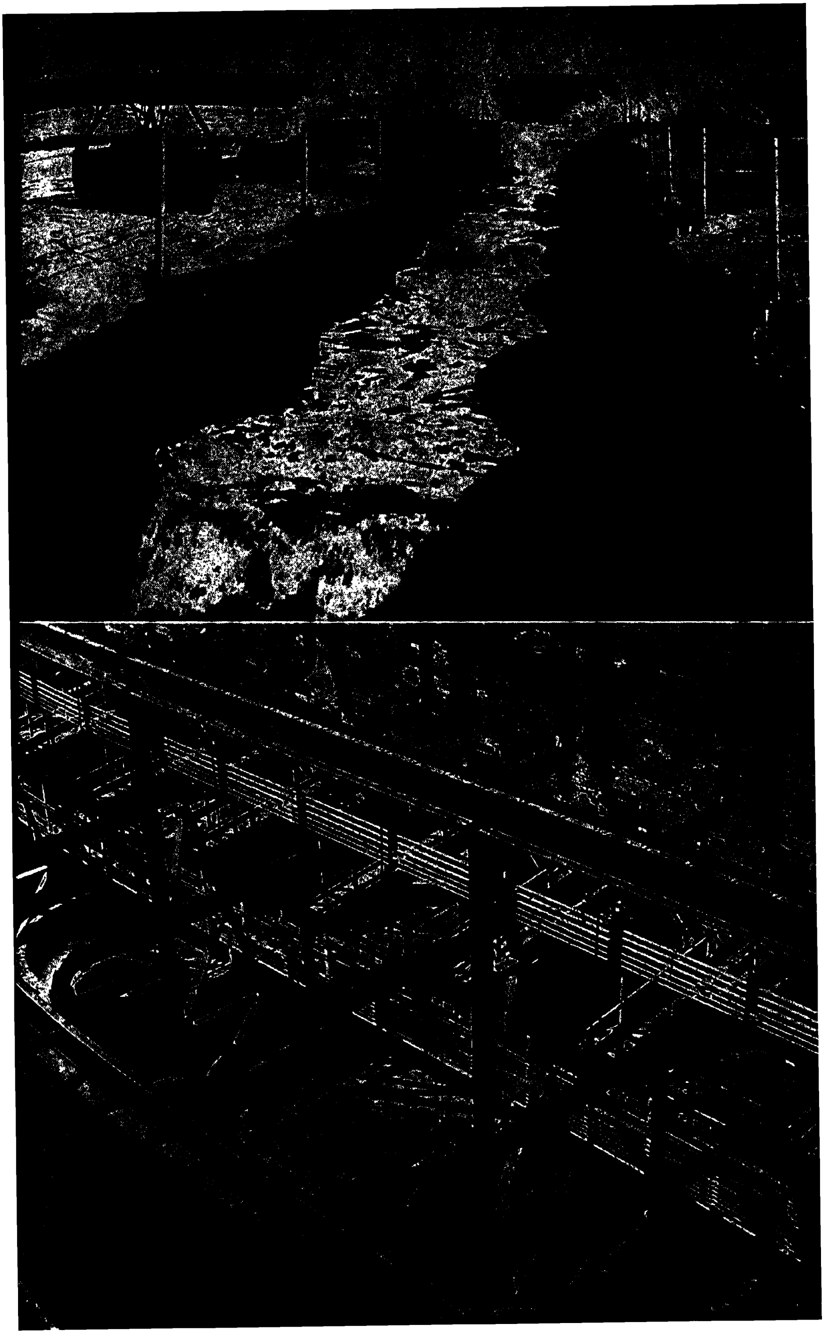
Bromine usually occurs as bromides, particularly as $MgBr_2$ and NaBr. These salts are found in certain mineral springs, those in Ohio containing from 3.4 to 3.9 per cent of $MgBr_2$. It also is found in the upper layers of beds of rock salt. The potash beds of Stassfurt, Germany, supplied the world for many years; and to a smaller extent the salt brines of Michigan, Ohio and West Virginia.

Recently, however, due to the enormous quantities of bromine consumed in lead gasoline containing tetraethyl lead (603) the Atlantic Ocean has become the chief source. Sea-water contains 67 parts of bromine (*as bromides*) per 1,000,000 of sea-water.

**602. Bromine from Sea-water.**—Following preliminary operations during 1931–1934, the Ethyl-Dow Chemical Company constructed a plant at Kure Beach, North Carolina, on a peninsula bounded by the Atlantic Ocean and the Cape Fear River. By

*Courtesy of the Ethyl-Dow Chemical Company*→

FIG. 191. The extraction of bromine from sea-water. *Top:* ocean water intake. *Bottom:* tanks of bromide-bromate solution, step *e.* Note the flume of incoming raw sea-water elevated above the tanks.



this arrangement sea-water received into the plant can be discharged into the river and carried 12 miles down the coast so as not to enter the plant again.

**a. Ocean water intake.** 150,000 gallons of sea-water per minute is pumped from the ocean into a storage pond where the warm sun heats it before it enters the plant.

**b. Regulation of acidity.** At the point where water from the pond is pumped into the plant, the sea-water is rendered slightly acid with $H_2SO_4$ (actually, pH 3.5, see section **232**), to prevent reaction between the sea-water and chlorine, which will subsequently be added, in accordance with the scheme:

$$Cl_2 + H_2O \rightarrow HCl + HClO.$$

**c. Displacement.** As soon as the proper acidity is reached in the pipe, chlorine is run in from one-ton chlorine cylinders. Displacement occurs:

$$Cl_2 + 2NaBr \rightarrow 2NaCl + Br_2.$$

Out of the 67 parts of Br per 1,000,000 being treated by this process, 95 per cent is removed.

**d. Blowing-out tower.** The water passes into a blowing-out tower where it is caused to flow in 3,200 small streams past a counter-current of air. Beyond this point the spent sea-water is discharged into the river.

**e. Absorption towers.** Meanwhile, the air, now laden with bromine, passes into absorption towers. Here the bromine is removed from the air by a solution of sodium carbonate (soda ash) according to the equation:

$$\underset{\text{soda ash}}{3Na_2CO_3} + 3Br_2 \rightarrow \underset{\text{bromide}}{5NaBr} + \underset{\text{bromate}}{NaBrO_3} + 3CO_2 \uparrow.$$

Each absorption tower consists of nine chambers in series. The carbonate solution is sprayed from one chamber to the next, consecutively; and the fresh soda ash is introduced into the chamber farthest from the blowing-out tower.

**f. Liberation of bromine.** The bromide-bromate solution is treated with sulfuric acid to liberate the bromine. This is a process used for many years in the recovery of bromine from brines:

$$NaBrO_3 + 5NaBr + 3H_2SO_4 \rightarrow 3Na_2SO_4 + 3H_2O + 3Br_2 \uparrow.$$

The free bromine vapors are steamed out of the acid solution and condensed to liquid bromine. Its subsequent treatment for use in gasoline containing tetraethyl lead is described in section **606**.

**603. Other Methods for Preparing Bromine.**—

**a. By electrolysis of brines.** At Midland, Michigan, the brine pumped up from the underlying salt-beds is concentrated to crystallize out common salt; and the remaining liquor, known as *bittern*, is subjected to electrolysis, bromine being set free at the anode. Bromine is less active than chlorine, so it is largely liberated by the current before chlorine is set free.

**b. By the oxidation of HBr.** In the foregoing section (**602, f**) $Br^-$ is oxidized to $Br_2$ by the action of $NaBrO_3$. A reaction similar in principle to this may be carried out in the laboratory, using $MnO_2$ as the oxidizing agent:

$$2NaBr + 3H_2SO_4 + MnO_2 \rightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Br_2 \uparrow.$$

However, bottles of liquid bromine are available in most laboratories.

**c. By displacement with $Cl_2$.** This treatment, often used on brines, is analogous to that already described for sea-water (**602, c-f**). The solution of bromide-bromate may be evaporated to dryness, and the dry salt shipped to a distant consumer, who can add sulfuric acid as bromine is needed.

In 1939 there was 14,000 tons of bromine recovered from sea-water at Kure Beach, North Carolina, and 5,000 tons of bromine obtained from Michigan and Ohio-West Virginia brines. Searles Lake is also to produce 1,500 tons annually.

**604. Physical Properties.**—Bromine is a dark-red liquid which boils at 58.5°. Bromine and mercury are the only elements which are liquid at ordinary temperature, although gallium and cesium liquefy a few degrees above room temperature. The specific gravity of bromine is about 3.18. About 4 parts of bromine are soluble in 100 parts of water. The vapor of bromine possesses a dark-red color and a very disagreeable odor; it attacks the eyes very painfully and produces great irritation when inhaled. When taken internally it acts as an irritant poison, and when brought in contact with the skin it produces sores which are difficult to heal.

**605. Chemical Properties.**—In its chemical deportment bromine resembles chlorine, but is less active. Thus, it combines directly with certain metals and non-metals, though its action is not as energetic as that of chlorine. Bromine also acts as a bleaching and oxidizing agent, but less quickly than does chlorine. At 228°, the density of bromine vapor is 5.525 (air = 1), showing that the molecule is diatomic, $Br_2$. At 1,050°, however, it begins to dissociate into monatomic molecules:

$$Br_2 \rightleftarrows 2Br.$$

**606. Uses.**—The demand for bromine has increased enormously in recent years because of the fact that it is added in the form of ethylene dibromide ($C_2H_4Br_2$) to ethyl gasoline, *i.e.*, to gasoline containing tetraethyl lead, $Pb(C_2H_5)_4$. About two cubic centimeters of ethylene dibromide is added to each gallon of ethyl gasoline. The ethylene dibromide is used to furnish bromine for transforming the lead of the tetraethyl lead into lead bromide; otherwise the free lead would injure the ignition-points.

The ethylene dibromide is manufactured at Kure Beach, North Carolina along with the bromine. The steps are:

$$\underset{\substack{\text{ethyl}\\\text{alcohol}}}{C_2H_5OH} \xrightarrow[H_3PO_4\text{ catalyst}]{-H_2O} \underset{\text{ethylene}}{C_2H_4} \xrightarrow[\text{from 602, f}]{+Br_2} \underset{\substack{\text{ethylene}\\\text{dibromide}}}{C_2H_4Br_2}.$$

Bromine is used also in the manufacture of coal-tar dyes; in "bromide" sedatives as KBr or NaBr in medicine; in silver photographic emulsions as AgBr; and in the manufacture of tear gases (lachrymators) such as bromo-acetone. "Solidified bromine" consists of sticks of siliceous earth (*kieselguhr*, 470) with size or molasses, burned until coherent, and then soaked in bromine. The porous material absorbs as much as 75 per cent of its own weight of the liquid.

**607. Hydrogen Bromide.**—Hydrogen bromide is obtained by the hydrolysis of phosphorus tribromide. In practice this consists in dropping liquid bromine upon a mixture of wet sand with one-third its weight of red phosphorus. The off-gas is passed through a tube of red phosphorus to catch any bromine vapor which might escape.

HBr cannot be prepared by treating a bromide with strong sulfuric acid, since $SO_2$ and $Br_2$ are also obtained (595, e). It can be prepared, however, by heating a bromide with phosphoric acid:

$$KBr + H_3PO_4 \rightarrow KH_2PO_4 + HBr \uparrow.$$

Hydrogen bromide is very similar to hydrogen chloride, but is not so stable. It is a colorless gas with a sharp odor. It is extremely soluble in water, forming an active acid, hydrobromic acid. Its salts are called **bromides**.

## IODINE $^{126.92}_{53}I$

**608. History and Occurrence.**—Iodine was discovered in 1812 by Courtois, a manufacturer of saltpeter, near Paris, who obtained it from the mother-liquor of salts produced from burnt seaweed, or **kelp**.

The liquid was heated with sulfuric acid in a retort, "a vapor of a superb violet color" being obtained, which condensed in the form of brilliant crystals. The element was subsequently examined by Davy, and much more in detail by Gay-Lussac, who established its elementary nature and first proposed the name iodine (Greek, *violet*) on account of the color of its vapor.

Iodine occurs in combination in small quantities, but widely distributed, both in the organic and inorganic kingdoms. It occurs in sea-water, in sea plants and sea animals, and in the thyroid gland of man and animals. Formerly, the only commercial source of iodine was seaweed, which was collected along the rocky coasts of Scotland, Ireland, and France. Certain sea plants, in growing, extract iodine from water. Thus, the giant sea plants, known as **kelp**, which grow along the Pacific coast, contain not only potassium chloride but a small quantity of iodides.

Chile has been the leading producer of iodine for many years, **sodium iodate,** $NaIO_3$, being found in saltpeter. Also, substantial quantities have come from several other countries. 150 tons is produced each year in the United States from California brines and seaweed. U. S. import fluctuates widely from year to year: for instance, 1,000 tons was imported in 1937, and only 100 tons in 1939.

**609. Preparation.—**

**a. From Chile saltpeter.** The mother-liquor remaining after crystallizing $NaNO_3$ from a solution of Chile saltpeter is treated with sodium bisulfite and sodium sulfite:

$$2NaIO_3 + 2NaHSO_3 + 3Na_2SO_3 \rightarrow 5Na_2SO_4 + H_2O + I_2.$$

The precipitated iodine is washed on filters made of coarse canvas or bagging, and is then subjected to pressure to remove water.

This iodine is purified by distilling the solid; the vapor condenses directly to the solid state without first liquefying. This is an example of **sublimation.**

**b. From Brines at Long Beach, California.** Iodides occur in brackish waters from oil wells in southern California. By treating this brine with nitrous acid, the iodine is liberated. It is absorbed in activated charcoal, and gives up the iodine when heated.

Iodine can also be liberated by treating the iodides with chlorine.

**c. Laboratory Method.** Flakes of solid iodine are a common sight about the laboratory, so that it is rarely prepared there.

The laboratory method consists in heating a mixture of sodium iodide and moderately concentrated sulfuric acid with an oxidizing agent, $MnO_2$:

$$MnO_2 + 2NaI + 3H_2SO_4 \rightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + I_2 \uparrow.$$

This, too, is the basis of a commercial method for extracting iodine from the ashes of seaweed.

**610. Physical Properties.**—Iodine is a shining, blackish-gray solid, which crystallizes in the rhombic system. It is the heaviest of the halogens, having a specific gravity of 4.948 at 17° (Stas). Iodine melts at about 113.5° and boils at 183°, giving a violet vapor which turns blue on strongly heating. Iodine is sparingly soluble in water. The best solvents for iodine are alcohol, carbon disulfide, chloroform, and an aqueous solution of potassium iodide (or other iodides). An alcoholic solution of iodine is brown in color, probably due to feeble union with the solvent. Carbon disulfide and chloroform solutions of iodine are violet. Iodine is very soluble in a solution of an iodide, owing to chemical action between the iodide and iodine:

$$KI + I_2 \rightleftarrows KI_3.$$

"Tincture of iodine" consists of iodine, potassium iodide, and alcohol.

*A trace of iodine colors starch "solution" a deep blue.* This is a most delicate test for the element, the chemist being able to detect 1 part of iodine in 5 million parts of water.

**611. Chemical Properties.**—In its chemical properties, iodine resembles chlorine and bromine, but is less active, being displaced from iodides by $Cl_2$ and $Br_2$. It unites directly with many of the metals and non-metals, giving off both heat and light: *e.g.*, white phosphorus soon bursts into flame when brought in contact with iodine. Chlorine and bromine combine with hydrogen much more readily than does iodine. The element, like chlorine and bromine, interacts with solutions of soda and potash (**602, e**). Iodine is an oxidizing agent.

The specific gravity of iodine vapor shows that it is diatomic up to 700° (*i.e.*, $I_2$); above this temperature the density diminishes, until at 1700° the iodine is monatomic.

**612. Uses.**—Iodine is used in the manufacture of certain coal-tar dyes, organic compounds, iodoform ($CHI_3$), KI, and NaI; in medicine, photography, and in chemical analysis. "Tincture of iodine" is effective in reducing certain swellings and as a germicide.

Iodine is an essential constituent of the animal body. It is estimated that there are approximately 20 milligrams in the body of a normal adult, about one-half of which is in the thyroid gland near the Adam's apple in the form of a hormone, **thyroxine**. Thyroxine was isolated in 1926 by E. C. Kendall from the thyroid glands of thousands of slaughtered cattle in the Chicago stock yards. Subsequently C. R. Harrington synthesized it. Its for-

*Courtesy of Westinghouse*→

mula is given in Fig. 192. A single milligram of this catalyst accelerates the body metabolism sufficiently to produce 400,000 milligrams of carbon dioxide.

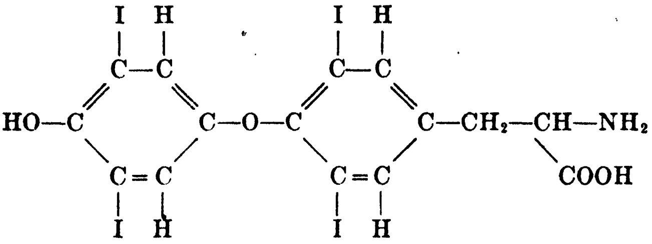


FIG. 192. Thyroxine.

It is very important to keep the thyroxine content of the body properly regulated. Subnormal quantities give rise to **goiter** or to **cretinism**, evidenced by lowered muscular activity and a dullness of mind; excess quantities of thyroxine produce **exophthalmic goiter,** symptoms of which are an enlarged thyroid gland, protruding eyeballs, palpitation of the heart, and anemia.

Ocean breezes carry sea-water inland several hundred miles, so that iodides from sea-water are present in the crops in those regions near the sea, and are found in spinach, lettuce, string beans; also in butter, milk, and salt-water fish. On the other hand, localities isolated from sea-water, such as the Alps, the Great Lakes and the Rocky Mountain regions, have an insufficiency of iodides in their crops and drinking water. As might be expected, there is a marked prevalence of goiter and cretinism in these regions. For consumption in these regions, "iodized salt" containing a fraction of a per cent of potassium iodide is sold, in order to supply the body with sufficient iodine to prevent goiter.

**613. Hydrogen Iodide.**—Hydrogen iodide, like hydrogen bromide, is prepared by hydrolysis of phosphorus halides by dropping water upon a mixture of red phosphorus and iodine:

$$PI_3 + 3HOH \rightarrow 3HI + H_3PO_3.$$

As the HI is evolved, it is passed through a U-tube containing moistened red phosphorus to absorb any iodine which may escape from the generator flask.

An aqueous solution of HI may be prepared by bubbling $H_2S$ into water containing iodine in suspension.

HI cannot be prepared by the interaction of an iodide with concentrated sulfuric acid, since the HI reacts further to form $H_2S$ and $I_2$ (**595, e**).

Hydrogen iodide, like HCl and HBr, is a colorless gas with a sharp odor; it dissolves readily in water to form highly ionized hydriodic acid, $H^+ + I^-$. This aqueous solution does not keep well. Hydrogen iodide dissociates into $H_2$ and $I_2$ upon heating; at 448° the mixture contains 79 per cent HI and 21 per cent $H_2$ and $I_2$. The salts of hydriodic acid are called **iodides.** KI and NaI are extremely soluble in water, but $PbI_2$ (yellow), AgI, $Hg_2I_2$, and $HgI_2$ (scarlet) are practically insoluble.

### OXIDES AND OXY-COMPOUNDS OF THE HALOGENS

**614. General.**—Table 118 summarizes our knowledge of the oxygen compounds of the halogens. Subsequently, the more important of these will be described.

TABLE 118. OXY-COMPOUNDS OF THE HALOGENS

| OXIDES | OXY-ACIDS | | | NOMENCLATURE | |
|---|---|---|---|---|---|
| | | | | acids | salts |
| $F_2O$; $(F_2O_2)$; $F_2O_3$ | HClO | HBrO | HIO | hypo-ous | hypo-ite |
| $Cl_2O$; $ClO_2$; $Cl_2O_7$ | $HClO_2$ | $(HBrO_2)$ | $(HIO_2)$ | -ous | -ite |
| $(Br_2O)$; $(BrO_2)$ | $HClO_3$ | $HBrO_3$ | $HIO_3$ | -ic | -ate |
| $I_2O_4$; $I_2O_5$ | $HClO_4$ | | $HIO_4$ | per-ic | per-ate |
| | | | $H_5IO_6$ | | |

*Question:* Insert the valences for each halogen in the above formulas. ( ) indicates that the compound is unstable.

**a. Fluorine.** Of the oxides of fluorine, $F_2O$ is a stable gas at room temperature; it is a powerful oxidizing agent. $F_2O_2$ is unstable above −100°. There are no oxy-acids of fluorine.

**b. Chlorine.** Chlorine and oxygen do not combine directly, but their union can be accomplished in the presence of a metallic oxide. As a rule, the oxygen compounds of chlorine are unstable, some of them being dangerously explosive: *e.g.*, $Cl_2O$ and $ClO_2$. Perchloric acid is the most stable of the oxy-acids of chlorine. The oxygen compounds of chlorine are powerful oxidizing agents. Thus, $Cl_2O$, $ClO_2$, $HClO_3$, and $HClO_4$ cause such substances as paper and wood to inflame. $HClO_2$ is known only in solution; salts (chlorites) of the acid have been prepared.

**c. Bromine.** The two oxides of bromine have only recently been prepared; they are both unstable. Bromous acid, $HBrO_2$, is so unstable that it has never been prepared except momentarily.

On the other hand, **hypobromous acid**, HBrO, and **bromic acid**, $HBrO_3$, are well known, being similar to the corresponding compounds of chlorine.

The salts of these acids may be prepared by methods similar to those used for the corresponding chlorine compounds. When bromine is added to cold, dilute potassium hydroxide solution, potassium hypobromite is formed, and when the solution is heated potassium bromate is formed:

$$2KOH + Br_2 \rightarrow KBr + KBrO + H_2O,$$
$$3KBrO \rightarrow KBrO_3 + 2KBr.$$

Bromic acid oxidizes iodine to iodic acid, which shows that the affinity of iodine for oxygen is greater than that of bromine:

$$2HBrO_3 + I_2 \rightarrow 2HIO_3 + Br_2.$$

**d. Iodine.** $I_2O_4$ and $I_2O_5$ are both stable even at somewhat elevated temperatures. The pentoxide may be obtained as a white powder by heating iodic acid:

$$2HIO_3 \rightarrow H_2O + I_2O_5.$$

It is the anhydride of iodic acid, just as $N_2O_5$ is the anhydride of nitric acid.

Hypoiodous acid, HIO; iodic acid, $HIO_3$; and periodic acid, $HIO_4$, $2H_2O$, are also known. Iodous acid, $HIO_2$, on the other hand, is too unstable to have been isolated.

The iodates of the alkali metals may be prepared by treating a hot solution of an alkali with finely divided iodine (see Chlorates). Iodic acid may be prepared by oxidizing iodine:

$$5HClO + H_2O + I_2 \rightarrow 2HIO_3 + 5HCl.$$

In practice, chlorine is passed through iodine suspended in water.

Sodium iodate ($NaIO_3$) and sodium periodate ($NaIO_4$) occur in Chile saltpeter.

### OXIDES AND OXY-ACIDS OF CHLORINE

**615. The Oxides of Chlorine.**—

**a. Chlorine monoxide, $Cl_2O$.**

Chlorine monoxide is a brownish-yellow gas, condensing to a dark-yellow liquid. The gas has a peculiar penetrating odor and irritates the eyes. This oxide is very explosive, many oxidizable substances catching fire in its presence:

$$2Cl_2O \rightarrow 2Cl_2 + O_2.$$

Chlorine monoxide is the anhydride of hypochlorous acid, being readily soluble in water:

$$Cl_2O + H_2O \rightleftarrows 2HClO.$$

**b. Chlorine dioxide, $ClO_2$,** is formed when powdered potassium chlorate is added gradually to concentrated sulfuric acid [*Care!*]:

(1) $$KClO_3 + H_2SO_4 \rightarrow KHSO_4 + HClO_3,$$

(2) $$3HClO_3 \rightarrow 2ClO_2 + HClO_4 + H_2O.$$

Chlorine dioxide is a heavy gas with a dark-yellow color, which condenses to a dark-red liquid. The compound must be handled with great care as it will explode if organic matter is present. It is, of course, a powerful oxidizing agent. Thus, a mixture of $KClO_3$ and sugar ($C_{12}H_{22}O_{11}$) may be ignited by adding a drop of concentrated sulfuric acid. [*Care! Avoid friction in preparing the mixture.*]

**c. Chlorine heptoxide.** This oxide is the anhydride of perchloric acid, and may be prepared by dehydrating that acid with cool $P_2O_5$:

$$2HClO_4 \xrightarrow[\text{cool}]{P_2O_5} Cl_2O_7 + H_2O.$$

Chlorine heptoxide is a colorless oily liquid, boiling at 82°. Under certain conditions the substance explodes with great violence.

### 616. Hypochlorous Compounds.—

**a. Hypochlorous acid.** This acid may be obtained by dissolving chlorine monoxide in water (**614, a**) or by dissolving chlorine gas in water:

$$Cl_2 + H_2O \rightarrow HClO + HCl.$$

Hypochlorous acid is a weak acid; it is unstable even in dilute aqueous solutions, breaking down into hydrochloric acid and either oxygen or chloric acid. (Write equations.)

**b. Sodium and potassium hypochlorite.** Salts of hypochlorous acid are prepared by passing chlorine into *cold, dilute* solutions of hydroxides (or alkali carbonates). If the solutions are not cold, the KClO reacts further to form chlorates and chlorides (32):

$$\begin{array}{l} 2KOH + Cl_2 \rightarrow KClO + H_2O + KCl \\ \qquad\qquad\qquad\qquad\quad \vdots \\ \qquad\qquad\qquad\qquad 3KClO \xrightarrow[\text{warm}]{} KClO_3 + 2KCl. \end{array}$$

A solution of KClO and KCl is called *eau de Javelle* (Javelle water), because it was first prepared at Javelle, a suburb of Paris, in 1792. A solution of the corresponding sodium salt is called *Labarraque's solution* (Labarraque, 1820). The hypochlorite is the active component in both solutions. At the present time, "Javelle water" contains the sodium salts. *Dakin's* and *Carrel's solutions,* which are similar to Javelle water, were used extensively during the Great War for cleansing deep wounds. Hypochlorites may also be formed by electrolysis; *e.g.*, if a solution of KCl is electrolyzed, the $Cl_2$ will react with the KOH to form KClO and $KClO_3$ in accordance with the foregoing equations.

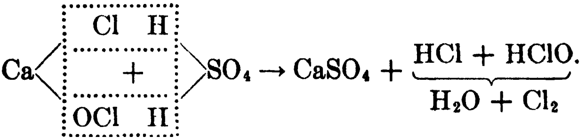
**c. Bleaching powder, chloride of lime, $CaOCl_2$.** This highly important substance was prepared by Tennant in 1799, who absorbed chlorine in dry calcium hydroxide (slaked lime).

Bleaching powder then sold for £140 per ton. It is prepared on a very large scale by conducting chlorine gas into a series of large rooms, over the floors of which slaked lime is spread:

$$Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O.$$

Bleaching powder is a yellowish-white solid. High-grade specimens contain 36 per cent of "available chlorine."

When treated with strong acids, it yields chlorine:



$$Ca\left\langle \boxed{\begin{array}{cc} Cl & H \\ + & \\ OCl & H \end{array}} \right\rangle SO_4 \rightarrow CaSO_4 + \underbrace{HCl + HClO}_{H_2O + Cl_2}.$$

Bleaching powder is used as a disinfectant. For bleaching vegetable fibres in the textile and paper industries, liquid chlorine has largely displaced it. In 1939 there were 10,573 tons of lime used for liquid and powdered bleaches, exclusive of the bleach used for paper manufacture.

**617. Chlorous Acid, $HClO_2$.**—A solution of chlorous acid may be prepared by treating a solution of barium chlorite, $Ba(ClO_2)_2$, with sulfuric acid and then filtering off the precipitate of barium sulfate:

$$Ba(ClO_2)_2 + H_2SO_4 \rightarrow BaSO_4 \downarrow + 2HClO_2.$$

The anhydrous acid is unknown, for the compound is very unstable. Its anhydride, $Cl_2O_3$, is also unknown.

Chlorites are unstable oxidizing agents and are liable to start combustion or to explode when rubbed with a combustible material such as sulfur.

**618. Chloric Acid, $HClO_3$.**—Chloric acid is the most important member of the series of the oxyacids of chlorine. It can be prepared in the laboratory by treating certain chlorates with mineral acids. Thus, when a solution of barium chlorate, $Ba(ClO_3)_2$, is decomposed by sulfuric acid, a solution of chloric acid is obtained:

$$Ba(ClO_3)_2 + H_2SO_4 \rightarrow BaSO_4 \downarrow + 2HClO_3.$$

The $BaSO_4$ is filtered off and the solution evaporated *in vacuo* over $H_2SO_4$. When the residue is concentrated beyond 40 per cent of $HClO_3$, or when the solution is heated, the acid decomposes:

$$3HClO_3 \rightarrow HClO_4 + 2ClO_2 + H_2O.$$

Chloric acid is therefore very unstable, being a powerful oxidizing agent. Like concentrated nitric acid, it may set fire to straw, etc. (Compare the two acids in other respects.)

**Chlorates**, the salts of chloric acid, are very important compounds, particularly the sodium and potassium salts. They are prepared commercially by electrolysis of warm solutions of alkalies (**614, b**), the anode and cathode products being allowed to mix:

$$6KOH + 3Cl_2 \xrightarrow[\text{electrolysis}]{70^\circ} KClO_3 + 5KCl + 3H_2O.$$

**They are also formed in accordance with this same equation when chlorine is led into hot, concentrated solutions of alkali or alkaline earth hydroxides.**

**Chlorates are powerful oxidizing agents, many of them being dangerously explosive; hence the use of $KClO_3$ in the manufacture of matches, flash-light powders, oxygen, and fire-works.**

**619. Perchloric Acid, $HClO_4$.**—Richards and Willard prepared perchloric acid as a colorless liquid by treating a saturated solution of sodium perchlorate with hydrochloric acid (sp. gr. 1.2):

$$NaClO_4 + HCl \rightleftarrows NaCl \downarrow + HClO_4.$$

The liquid is decanted off, and carefully distilled under reduced pressure. Under a pressure of 18 mm., the acid boils at 16°. It combines energetically with water to form several hydrates: *e.g.*, $HClO_4, H_2O$. Perchloric acid is a powerful oxidizing agent. Thus, it inflames paper and wood and causes serious burns when brought in contact with the skin. In dilute solutions, however, it does not exhibit oxidizing properties. Its anhydride is chlorine heptoxide, $Cl_2O_7$.

The salts of perchloric acid, called **perchlorates**, *are the most stable salts of the oxy-acids of chlorine.* Potassium perchlorate may be obtained by heating potassium chlorate just above its melting point; at a higher temperature oxygen is freely formed (32):

$$4KClO_3 \xrightarrow{>368^\circ} 3KClO_4 + KCl$$

$$\xrightarrow{>400^\circ} 3KCl + 6O_2 \uparrow.$$

The chloride is much more soluble in water than is the perchlorate, so that the two salts may be separated by crystallization.

Perchlorates, like chlorates, nitrates, and acetates, are soluble in water. $KClO_4$ and $RbClO_4$ are sparingly soluble in water, but practically insoluble in absolute alcohol. This property is made use of in the estimation of potassium in quantitative analysis. Perchloric acid, also, is used in analytical chemistry, as an oxidizing agent. Anhydrous perchlorates are good dehydrating agents, a mixture of barium and magnesium perchlorates being particularly efficient.

## QUESTION REVIEW

I. THE HALOGEN FAMILY (595).

1. Summarize the members of group VII-B under the headings: occurrence, preparation, physical properties, chemical properties, halogen acids, oxy-acids.

**a. Fluorine** (596–599).

2. Give four equations illustrating the preparation and properties of fluorine and its compounds.
3. Of what use is: cryolite, fluorspar, hydrogen fluoride, a gutta-percha bottle?

**b. Chlorine** (600).

4. Give six equations illustrating the chemistry of chlorine and of hydrogen chloride. What is meant by a *chain reaction*?

**c. Bromine** (601–607).

5. Give in detail, with equations, the process for recovering bromine from sea-water. What is made from the free bromine, and what is its function in gasoline?
6. Give four other equations illustrating the chemistry of bromine.

**d. Iodine** (608–613).

7. Give the equation for the extraction of iodine from Chile Saltpeter.
8. What is: sublimation, kelp, an iodate, displacement, mother-liquor, activated charcoal, tincture of iodine, thyroxine, goiter, a halide, iodized salt?
9. Show by equations why HI and HBr cannot be prepared in a pure state by the interaction between a halide and concentrated sulfuric acid.

II. OXIDES AND OXY-ACIDS OF THE HALOGENS (614)

10. Draw up Table 118, inserting the valences of the halogens in the different compounds. Show which oxides are anhydrides, and the acid to which each is related.
11. State one fact about one oxide of each halogen. About one oxy-acid of each halogen.

III. OXIDES AND OXY-ACIDS OF CHLORINE: **oxides (615); hypochlorous acid (616); chlorous acid (617); chloric acid (618); perchloric acid (619).**

12. **State one important fact, such as preparation, property, use, etc., about each of the following: $ClO_2$, KClO, $KClO_3$, $CaOCl_2$, $Cl_2O_7$, $MgClO_4$, $HClO_2$, $HClO_4$, $Cl_2O$.**

13. Show by equations how each of the following reactions may go in two ways: (*a*) KOH + $Cl_2$; (*b*) electrolysis of KOH; (*c*) heating $KClO_3$.
14. Calculate the percentage of "available chlorine" in a specimen of pure $CaOCl_2$.
15. What experiments would you perform to differentiate between the following acids: hydrochloric, perchloric, chloric, hypochlorous.
16. Potassium perchlorate is practically insoluble in 95 per cent alcohol containing 0.2 per cent of perchloric acid. Explain fully why the presence of the acid lowers the solubility of the salt.

**Reading References:** Articles number 10, 69, 106, 133, 214, 231, 233 and 338 in the Appendix.

# PART IV: ORGANIC CHEMISTRY

Chain Compounds: hydrocarbons, including gasoline, rubber and plastics; other chain compounds, including acids, alcohols and esters

Ring Compounds: products from coal-tar

Plant Foods and Plant Products: photosynthesis; inorganic plant foods; carbohydrates, including sugars, starch, cellulose and its products

Animal Foods and Animal Products: proteins; carbohydrates and fats; vitamins, enzymes and hormones; protein fibers

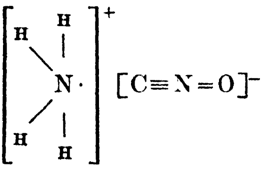
# CHAPTER XLI

# CHAIN COMPOUNDS

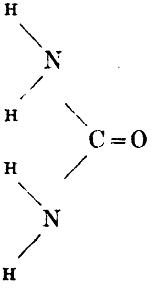
## PART I: HYDROCARBONS. GASOLINE. RUBBER. PLASTICS

**619. Organic Chemistry.**—Scarcely more than a century ago matter was divided into the dead and the living. Living matter, the carbon compounds found in plants and animals, was the product of a "vital force"; living matter could not, therefore, be synthesized by man. This notion was disproved by the German chemist F. Wöhler in 1828 when, upon heating ammonium cyanate, a compound formed from inorganic substances, he found it was transformed into urea, the nitrogenous waste material of the body:

Ammonium cyanate ($N_2H_4CO$)



Urea ($N_2H_4CO$)



These two substances, which contain the same atoms, but in different arrangement in space, are called **isomers.** Although the synthesis of urea broke down the mysterious barrier between the dead and the living, the convenient division into inorganic chemistry and organic chemistry has been retained to this day.

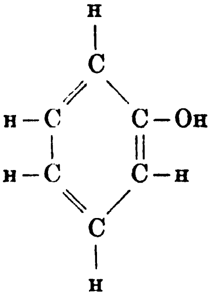
**Organic chemistry** is the chemistry of compounds containing carbon and hydrogen (*i.e.*, there are some inorganic carbon compounds such as $CO$, $CO_2$, $CaCO_3$, etc.). Organic compounds occur abundantly in all animal and plant life; in coal and petroleum which had their origin in plant life; and in such materials as dyes, drugs, explosives, plastics and rubber, made from these living materials or synthesized by man.

Now the number of organic compounds is several hundred thousand, whereas the number of all other compounds is approximately 30,000. For example, the elements C, H, O form at least a hundred thousand compounds; but the elements Cl, H, O form a scant dozen compounds. Why is this so? Why does carbon occupy this unique position?

As the story of organic chemistry unravels, we shall see that a variety of molecules is made possible by the formation of isomers (page 645) and the linking of carbon to carbon. In particular, carbon atoms may link in long chains, or interlock to form "rings":

$CH_3-CH_2-CH_2-CH_2OH$

butyl alcohol
(*a chain compound*)



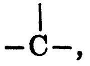
phenol
(*a ring compound*)

The former compounds are called **chain** or **aliphatic compounds**, since the fats possess this chain-like structure; the latter are called **ring, cyclic,** or **aromatic compounds.**

## SATURATED HYDROCARBONS

**620. The Methane Series.**—Hydrocarbons are compounds containing only carbon and hydrogen. This includes natural gas (methane), petroleum (octane and related compounds), rubber (related to isoprene), and coal-tar products (benzene, toluene, naphthalene, etc.).

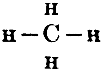
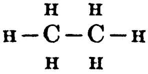
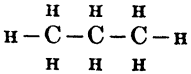
In all of these compounds **carbon has a valence of four.** The organic chemist often writes **structural formulas** for his molecules; in these carbon is written



$$\overset{|}{-C-},$$

which in a space model assumes the form of a tetrahedron with carbon at the center. One class of hydrocarbons, known as the **methane or paraffin series** has the general formula $C_nH_{2n+2}$. The first three members of this series are given in Table 119.

TABLE 119. THE METHANE SERIES (SATURATED HYDROCARBONS)

| | METHANE | ETHANE | PROPANE |
|---|---|---|---|
| Formula | $CH_4$ | $C_2H_6$ | $C_3H_8$ |
| Structural formula |  $\begin{array}{c}H\\H-C-H\\H\end{array}$ |  $\begin{array}{c}H\quad H\\H-C-C-H\\H\quad H\end{array}$ |  $\begin{array}{c}H\quad H\quad H\\H-C-C-C-H\\H\quad H\quad H\end{array}$ |
| M.P. | $-184°$ | $-172°$ | $-189.9°$ |
| B.P. | $-161.4°$ | $-88.3°$ | $-44.5°$ |
| Also written | $CH_4$ | $CH_3-CH_3$ | $CH_3-CH_2-CH_3$ |

Such a series is called a **homologous** (Greek, *corresponding*) **series.** The names of the hydrocarbons in this particular series end in **ane.** Each member differs from the member which precedes or follows it by one atom of carbon and two atoms of hydrogen ($CH_2$). Also, all four valences of the carbon are employed; for this reason these compounds are called **saturated hydrocarbons** to distinguish them from other hydrocarbon series where the carbon bonds are not fully employed (ethylene, acetylene and benzene series).

There is a gradual transition of properties as one passes up the methane series. For example, $CH_4$ to $C_4H_{10}$ are gases, the B.P. increasing as we pass from methane to propane; $C_5H_{12}$ to $C_{16}H_{34}$ are liquids; $C_{17}H_{36}$ and above are solids.

**621. Methane, or Marsh Gas, $CH_4$.**—This gas is formed in marshes by the decay of vegetable matter; also, it is the dreaded *firedamp* found in coal mines. Natural gas usually contains over 50 per cent methane. During the destructive distillation of wood and coal, methane is evolved; the coal gas used in many households contains about 30–40 per cent of methane by volume.

Methane is a colorless, odorless, tasteless gas, only slightly soluble in water. It forms a colorless liquid at −165° and solidifies at −186°. (Dem. 91, Section 270.)

In the methane molecule the carbon atom is situated at the center of a tetrahedron, with the four hydrogen atoms at the corners (similar to the diamond structure Fig. 159).

Like other paraffins (Latin, *parum,* little + *affinis,* affinity), methane is indifferent to most chemical reagents; in this respect it is wholly unlike the unsaturated hydrocarbons (**626**). For instance, the members of the methane series will not react at all with iodine; and reaction with chlorine and bromine must be brought about by light or heat. The resulting action in the latter case may be two-fold:

displacement: $CH_4 + 2Cl_2 \rightarrow C + 4HCl$
substitution: $CH_4 + Cl_2 \rightarrow HCl + CH_3Cl$ methyl chloride
$CH_4 + 2Cl_2 \rightarrow 2HCl + CH_2Cl_2$ methylene chloride
$CH_4 + 3Cl_2 \rightarrow 3HCl + CHCl_3$ chloroform
$CH_4 + 4Cl_2 \rightarrow 4HCl + CCl_4$ carbon tetrachloride

When hot turpentine is lowered into chlorine (Dem. 47, Section 136, *b*) dense black clouds of carbon indicate the reaction is displacement. A similar result is obtained when direct sunlight explodes a mixture of chlorine and methane. On the other hand, if the light is not too intense, reaction is more gradual and substitution products are obtained.

A mixture of methane and oxygen (or air) is extremely explosive, the maximum effect being obtained when 2 volumes of oxygen or 10 volumes of air are mixed with 1 volume of methane. The product of the explosion is **water and carbon dioxide; these are formed whenever a hydrocarbon burns:**

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2 + 213{,}500 \text{ cals.}$$

The blue flame of the Bunsen burner (Fig. 193), or of the domestic gas-range, are examples of burning methane.

c

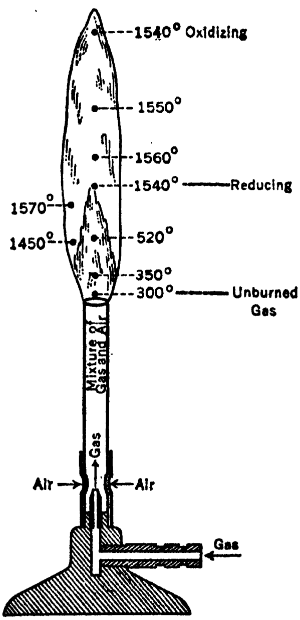


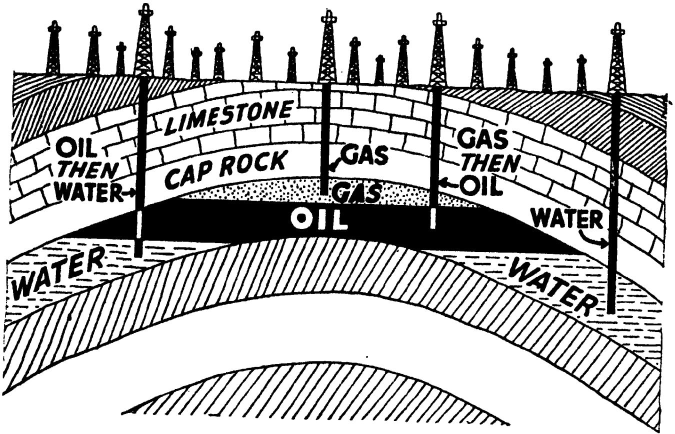
FIG. 193. The Bunsen burner.

**622. Petroleum.** Petroleum (Latin *petra*, rock + *oleum*, oil) has been known since ancient times.

The "Greek Fire" which held Constantinople impregnable from 330 A.D. to 1453 A.D., and thereby preserved Greek culture, may have been a self-igniting mixture of petroleum and quick-lime.

In 1857 Rumania produced 250 tons of petroleum from hand-dug wells, as a substitute for whale-oil and tallow illuminants. Acting on the advice of

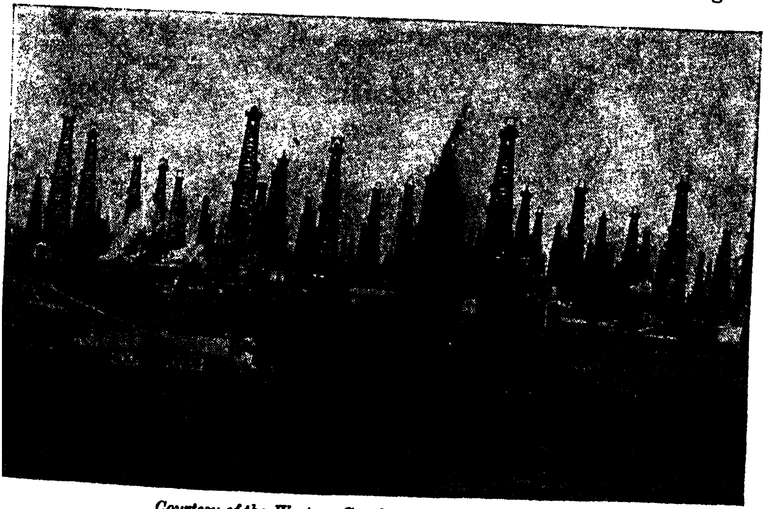
Professor Silliman of Yale University, an American business man hired E. L. Drake to *drill* for petroleum at Titusville, Pa., and in 1859 oil was struck. The petroleum boom started, and within three months 10,000 people had made their homes near the well.



*Courtesy of the American Petroleum Institute*

FIG. 194. Oil is where you find it.

**Location.** Petroleum is frequently associated with salty water or salt domes: the domes in Iran, for instance, rise a mile above the surrounding ter-



*Courtesy of the Western Geophysical Company and Standard Oil of Indiana.*

FIG. 195. Scientific prospecting for oil by seismograph recording of explosion waves.

rain, forming mountains several miles in diameter. "Wildcatting" for oil resources is only one-sixth as successful as scientific prospecting. In the United States, artificial earthquake waves are set up by exploding dynamite (Fig. 195); these are recorded on seismographs, and from the velocity of sound reflected from the oil-bearing rock, its position may often be determined within 20 feet.

**Drilling.** Rotary drills of tungsten carbide 2 feet in diameter chip through the hard rock. As the hole is made, pipe is lowered in sections, and cemented. A well 3 miles deep, such as was dug in 1939 in California, takes several months to drill and nearly 500 tons of pipe. Near the top a "Christmas Tree" of pipes is fastened, so that if the oil suddenly gushes forth, it can flow out through numerous pipes. It costs between $20,000 and $250,000 to drill each well, of which there were 350,000 in the United States in 1941. Here oil is classed as "wild game," for it belongs to the person who captures it first: this legal ruling has encouraged rapid drilling at the sacrifice of economic and planned exploitation. In Russia, Iran, and Iraq, on the other hand, the management is under governmental control.

TABLE 120. CRUDE PETROLEUM PRODUCTION (1939)
(in barrels)

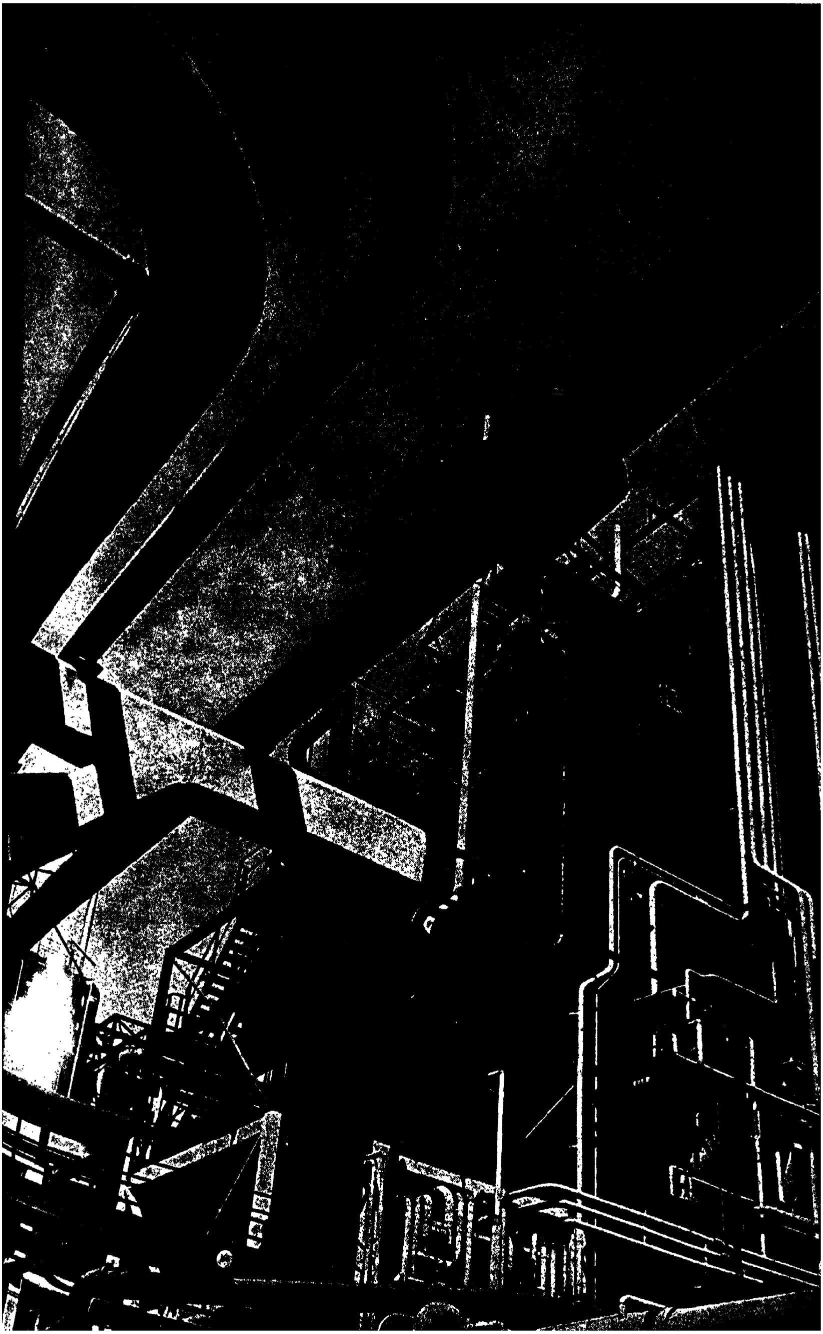
| | | | |
|---|---|---|---|
| United States | 1,264,256 | UNITED STATES | |
| Other North America | 69,971 | Pennsylvania grade | 27,175 |
| Venezuela | 205,956 | Oklahoma, Kansas, North Texas | 357,639 |
| Total Europe | 270,283 | California | 224,354 |
| Rumania | 45,996 | Texas, W., E., S. | 453,153 |
| U.S.S.R. | 212,500 | Illinois-Indiana | 95,725 |
| Total Asia | 205,284 | | |
| WORLD | 2,076,772 | | |

We also have vast deposits of the rock called **oil shale**. It is reported that the state of Indiana has over 450 trillion tons of the rock, and there are whole mountains of it in Colorado and in Utah. When heated in appropriate stills these shales yield from 10 to 50 gallons of oil per ton; but at present the expense of production is too high to compete with petroleum. In the future, however, they will be, no doubt, of great value.

**Pipelines.** 90 per cent of the oil in the United States is transported by pipelines, of which there are 150,000 miles for natural gas, 116,000 miles for crude oil, and 3500 miles for refined gasoline.

*Courtesy of Standard Oil of Indiana*

Modern, complex refining equipment, showing a high pressure tower system. In the foreground, products from the cracking furnace are piped to the stills. In the background are low pressure tower systems. This equipment processes crude petroleum directly to gasoline, kerosene, tractor fuel, furnace oil, fuel oil, gas and coke without redistillation on other equipment. (Photograph by Torkel Korling.)



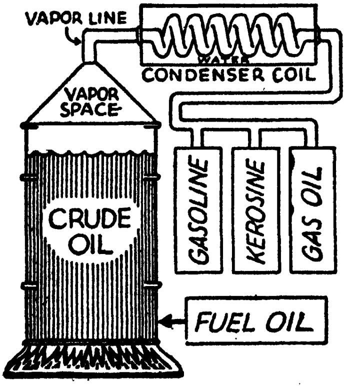
**Composition of Crude Oil.** Though there are literally hundreds of different hydrocarbons in natural petroleum, there is one simplifying feature: it is made up entirely of two elements, carbon and hydrogen.

Some samples of petroleum, such as those from the Pennsylvania fields, are composed almost entirely of hydrocarbons of the paraffin series and are therefore called "paraffin base oils." On distillation they yield a residue of solid paraffin. Other samples of petroleum, *e.g.*, those from California, yield a residue resembling natural asphalt; hence this type of petroleum is termed "asphalt base oils." The petroleum from the Midcontinent field yields both paraffin and asphaltic materials. The Borneo-Java petroleum contains much benzene and its homologues, and crude Mexican oils contain a great deal of sulfur.

The Rumanian oils contain a large fraction of light oils, and therefore give much gasoline.

TABLE 121. DISTILLATION FRACTION FROM PETROLEUM

| Name | Approximate Composition | Boiling-Point Range | Uses |
|---|---|---|---|
| Gases | $CH_4$–$C_4H_{10}$ | | Fuel; carbon-black |
| Petroleum Ether | $C_4$–$C_7$ | 35°– 80° | Solvent |
| Gasoline | $C_4$–$C_{13}$ | 40°–225° | Motor Fuel |
| Kerosene | $C_{10}$–$C_{16}$ | 175°–300° | Lighting; fuel |
| Middle Fractions (gas oil) | About 40% of the crude oil | 225°–375° | To "crack" into gasoline |
| Lubricating Oils | | | Lubrication |
| Vaseline | | 350° up | Lubrication |
| Paraffin | | | Candles; waterproofing |
| Tar Residue | | | Paving; roofing |
| Coke | | | Fuel |



*Courtesy of the American Petroleum Institute*

FIG. 196. Schematic representation of the distillation of petroleum.

The chief commercial products from petroleum are given above in table 121.

**Distillation.** The various products are separated by distillation. An average crude oil yields 25 per cent gasoline, 20 per cent kerosene, 10 per cent gas-oil, 25 per cent heavy paraffin oil, and 20 per cent residue. The vapor passes up through towers often containing plates which spread the liquids over their surface so that rising gases come into contact with some condensing liquid; this device gives a more efficient "cut" into the different fractions.

**Cracking.** The thermal decomposition of heavy oils into gasoline was carried out as early as 1860. From 1913 to 1925 a method designed by Burton was in use, and since then cracking in Cross or in Dubbs units at slightly elevated pressures (up to 50 atmospheres) and high temperatures (600° C.) have been in continuous operation. Besides breaking large molecules into smaller ones, the cracking process, which may be carried out in the presence of hydrogen (Bergius, see Section **623, b**), also transforms nearly half of the chain hydrocarbons into ring hydrocarbons (benzene, toluene), which are themselves better fuels than most chain compounds.

**Polymerization.** This is the reverse of cracking, for smaller gaseous hydrocarbon molecules will polymerize to form liquid gasoline. The Universal Oil Products Co., for instance, catalytically removes hydrogen (dehydrogenates) from butane ($C_4H_{10}$) at 500° C and 1 atmosphere pressure to form butene ($C_4H_8$); and then polymerizes and hydrogenates this at 200° C. and 15 atmospheres pressure to form isooctane ($C_8H_{18}$). 175,000,000 gallons of liquid **butane** and **propane** were converted into liquid gasoline by this process in 1940.

In addition, 19,000,000 gallons of these **petroleum gases** are used for city gas plants, 128,000,000 gallons for domestic use (*e.g.*, "Philgas," liquid propane and butane); and enormous quantities will soon be required by the new nitroparaffin and synthetic rubber industries (**625, 628**).

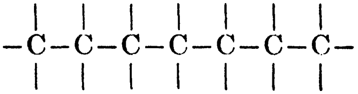
**Alkylation.** Branched-chain hydrocarbons make superior gasoline. Recently catalytic processes have been initiated for introducing methyl and other paraffin (also called alkyl) groups into straight chain hydrocarbons. The process is called *alkylation.*

**Purification.** Substances which form gums in the gasoline are removed by treatment with sulfuric acid (see Table 114, Section 590). The excess acid is removed with an alkali.

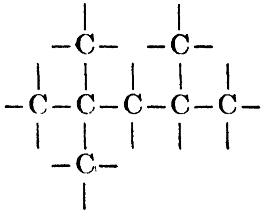
Subsequently, evil-smelling sulfur compounds (mercaptans) are removed chemically with $Pb_3O_4$ or NaOCl, or separated physically by filtering through activated charcoal or by extracting with solvents such as nitrobenzene, furfural, or phenol.

**Knock.** Detonation in dynamite travels up to 15,000 feet per second; but the flame in an automobile cylinder moves slowly and quietly, 25 to 250 feet per second. In poor-grade gasoline, however, the advancing flame suddenly accelerates after all but the last quarter of the gaseous mixture has burned; this quickly increases pressure manyfold, and a knock is heard.

It has been shown that the latter, rapid, reaction is a chain reaction (205). As little as 0.001 per cent tetraethyl lead, $Pb(C_2H_5)_4$, breaks these chains and prevents knock. The knock rating of a gasoline is measured by a steel diaphragm (bouncing pin) built into the test cylinder, which records the force of the knock electrically. Two hydrocarbons are used as standards (the H atoms are omitted for simplicity; there should be one on each free bond):



normal heptane
*octane number 0*
(knocks badly)



"isooctane"
*octane number 100*
(no-knock)

A modern gasoline with an "octane rating" (knock rating) of 80 gives the same violence of knock as a mixture containing 80 per cent isooctane and 20 per cent normal heptane.

Aviation fuel has an octane rating of over 100; and the automobile of the future will undoubtedly be re-designed to utilize this superior fuel. Isooctane cost $30 a gallon in 1934, but by 1940 the U. S. Navy had ordered 18,000,000 gallons of it.

**623. Synthetic Gasoline.**—Liquid gasoline may also be synthesized directly from coal, which indeed has supplied Germany with most of its gasoline today. The Germans employ the Fischer-Tropsch process. The advantages of the process are that it uses a stable catalyst; that it may be carried out in small units scattered over the countryside for military reasons; and that it requires the attention of relatively unskilled technicians. The Bergius process is somewhat cheaper, and is used in England; but it must be operated in enormous units controlled by highly trained chemists.

**a. The Fischer-Tropsch process.** Steam is passed over heated coal to form water-gas, which in turn is hydrogenated to form gasoline:

$$\underset{\text{coal}}{C} + H_2O \rightarrow CO + H_2$$

$$8CO + 17H_2 \rightarrow 8H_2O + \underset{\text{gasoline}}{C_8H_{18}}.$$

The German product, called **kogasin oil,** contains gasoline, kerosene, Diesel oil, and paraffin wax. The German plants were reported to have a capacity of 17,000,000 gallons in 1940.

**b. The Bergius process.** Coal is hydrogenated directly at 300 atmospheres pressure and 500° C.:

$$\underset{\text{coal}}{8C} + 9H_2 \rightarrow \underset{\text{gasoline}}{C_8H_{18}}.$$

England produced 1,300,000 barrels of synthetic gasoline by this process in 1937.

**624. Other Synthetic Fuels.**—Several other fuels have been substituted for gasoline in automobiles.

**Power alcohol** made by the fermentation of molasses or from potato starch (633) is a material of considerable importance. For example, the United Provinces of India require the admixture of up to 20 per cent alcohol with gasoline. The enormous quantities of molasses available in India could furnish power alcohol equivalent to 1,000,000,000 gallons of gasoline annually. Sweden, too, is developing power alcohol from the fermentation of sulfite pulp liquors, which potentially could replace 200,000,000 gallons of gasoline annually.

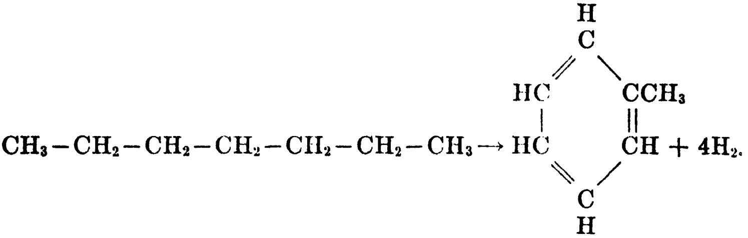
The European countries spent $50,000,000 subsidizing the addition of benzene to gasoline in 1937. However, the ultimate intent of this subsidy was to build up potential munition fatories using benzene derivatives for making explosives (645).

Several hundred thousand automobiles, buses and trucks in Europe during 1940–41 were operated on compressed gases. An alloy tank, weighing 115 pounds, filled with liquefied butane-propane is equivalent to 18 gallons of gasoline, and will propel an automobile over 200 miles before refilling.

Automobiles burning wood and charcoal also made their appearance in 1937–41. In 1939 wood substituted for 18,000,000 gallons of gasoline. The automobile converts the wood or charcoal into a sort of producer gas (499), which is then delivered to the cylinders through a special carbureter. France met 20 per cent of her gasoline needs in 1938 in this fashion. 30,000 wood-burning automobiles were operated in Stockholm in 1941.

**625. Products from Petroleum.**—Since 1939 petroleum has become an important raw material for many substances.

**Glycerine (631)** is consumed in large quantities, 10,000 tons annually, in the rayon and cellophane industries. The most important process (Neuberg) for manufacturing it is by the fermentation of sugar (*e.g.* black-strap molasses) in the presence of sodium bisulfite, which arrests the fermentation at this stage. Since 1938 another process, which involves chlorination of petroleum gases (*e.g.* propylene) has held some promise. **Nitroparaffins** such as $C_4H_9NO_2$, may be manufactured by the interaction of gaseous hydrocarbons with nitric acid vapor, in accordance with patents licensed to the Commercial Solvents Corporation by H. B. Hass of Purdue University. These nitroparaffins are used as a starting material for several hundred products, among them important solvents and explosives. **Synthetic rubber** (628) and **plastics** (629) are discussed subsequently. **Cyclic compounds** from petroleum open up a vast new field:



heptane toluene

The Shell Oil Co. completed a plant in 1940 for this process; it has a capacity of 10,000,000 gallons of toluene annually, giving 50,000 tons of T.N.T. explosive. Even **edible fats** have been made, in Germany, by oxidizing petroleum hydrocarbons made from coal; 40,000 tons of these synthetic fats were substituted for natural fats in 1939 for making **soap.**

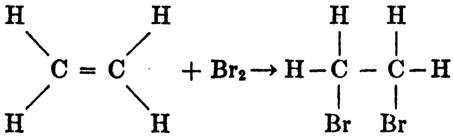
### UNSATURATED HYDROCARBONS

**626. Ethylene.**—Ethylene is the first member of an homologous series called the **olefant series** or **ethylene series,** having the general formula $C_nH_{2n}$. It is manufactured both on a laboratory and industrial scale by removing water from ethyl alcohol with syrupy phosphoric acid at about 160°:

$$\underset{\text{ethyl alcohol}}{C_2H_5-OH} \rightarrow \underset{\text{ethylene}}{C_2H_4} + H_2O.$$

Ethylene is a colorless gas with an ethereal odor. It burns with a very luminous flame, and is extremely explosive when mixed with oxygen. It is an anaesthetic.

In ethylene the carbon atoms are **unsaturated,** *i.e.*, they are connected by a double bond. Such a bond is a point of weakness in the molecule: as a result, ethylene is extremely reactive and combines directly with bromine or chlorine, forming addition products:

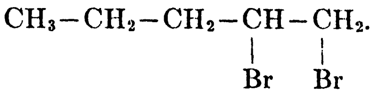


This reaction is industrially important in the manufacture of ethylene dibromide for counteracting the corrosive action of lead formed from "ethyl gas" (**602**).

### DEMONSTRATION 160. UNSATURATED COMPOUNDS

Materials: Two-liter flask containing a cc. of $Br_2$; amylene.

When a cc. of amylene, $CH_3 - CH_2 - CH_2 - CH = CH_2$, a substance similar to ethylene in that it possesses a double bond, is added to a flask of bromine, the hydrocarbon quickly decolorizes, as bromine is added to the double bond, forming



$$CH_3-CH_2-CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-\underset{\displaystyle Br}{\underset{|}{CH_2}}.$$

**627. Acetylene, $C_2H_2$.**—This is the first member of the acetylene series, $C_nH_{2n-2}$. It is formed from calcium carbide and water:

$$CaC_2 + 2HOH \rightarrow Ca(OH)_2 + C_2H_2 \uparrow .$$

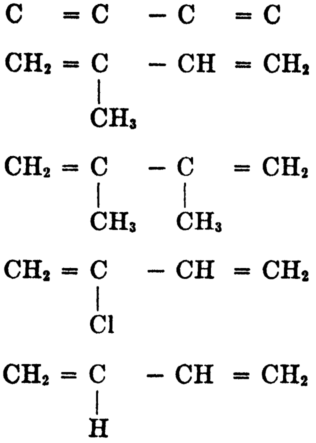
Acetylene is a colorless gas with a disagreeable odor (due to impurities). It is dangerously explosive; but when it is dissolved in acetone in a tank containing an absorbent material it may safely be transported; in this form it is used for oxy-acetylene torches.

Acetylene is unsaturated and has a triple bond, $H-C \equiv C-H$, so that it readily forms addition products such as acetylene tetrachloride, $C_2H_2Cl_4$, and the tetrabromide, $C_2H_2Br_4$. It also forms explosive metallic compounds known as **acetylides**: *e.g.*, copper acetylide, $Cu_2C_2, H_2O$, and silver acetylide, $Ag_2C_2, H_2O$. Acetylene is the raw material from which many of our synthetic products are made today (rubber, **628**; plastics, **629**).

When an electric discharge is passed through acetylene, or it is heated in contact with copper, it polymerizes to a fluffy brown solid known as **cuprene.**

**628. Rubber.**—Four centuries ago the white man found the Indians of South America playing ball with a strangely resilient, elastic material. Subsequently Joseph Priestley, of oxygen fame, discovered that rubber would erase lead-pencil marks; for this purpose it was imported in England as "Indian Rubber."

Rubber can be broken down into an unsaturated hydrocarbon called *isoprene* (Williams, 1860); this is closely related to the synthetic rubbers which appeared in volume during 1938–1940 (Fig. 197).



$C = C - C = C$ skeleton for rubber

$CH_2 = \underset{CH_3}{\underset{|}{C}} - CH = CH_2$ isoprene (natural rubber)

$CH_2 = \underset{CH_3}{\underset{|}{C}} - \underset{CH_3}{\underset{|}{C}} = CH_2$ 2–3-dimethyl butadiene

$CH_2 = \underset{Cl}{\underset{|}{C}} - CH = CH_2$ Neoprene, Perbunan, Buna N, Sovprene

$CH_2 = \underset{H}{\underset{|}{C}} - CH = CH_2$ butadiene, Butyl rubber, Ameripol, Buna, etc.

FIG. 197. Rubber monomers, natural and synthetic.

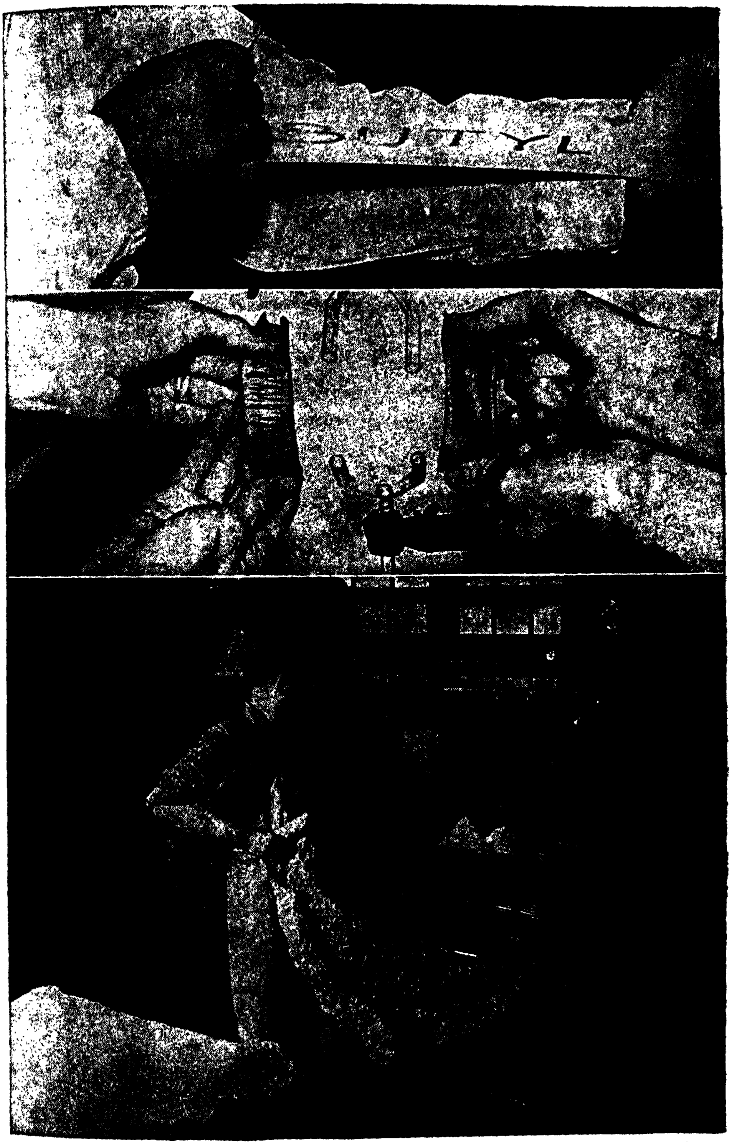
Butane is the 4-carbon paraffin, *i.e.*, $C_4H_{10}$. Butadiene has this same general form, but contains two double bonds (*di-ene*).

During 1914–18 Germany succeeded in making 2350 tons of 2–3-dimethyl butadiene rubber, but the product was not very successful. In 1926 the duPont Company became interested in some work by Father Nieuland of Notre Dame University on the polymerization of acetylene, followed by addition of HCl. With this research as a starting point, Carrothers carried on a series of investigations which led to the synthetic rubber Neoprene. Other polymerization studies by Carrothers culminated in the development of the synthetic fiber Nylon (663).

In recent years tremendous strides have been made in synthetic rubber manufacture, and by 1940 butadiene rubber made its appearance in the United States. Each country now manufactures butadiene from her most abundant resources. The United States uses butane from petroleum; Germany and Italy use acetylene from coal and limestone; while Russia ferments potato starch and grain to butyl alcohol.

The steps employed by the Standard Oil Company of New Jersey are:

$$\overset{\text{butane}}{CH_3-CH_2-CH_2-CH_3} \rightarrow CH_3-CHOH-CH_2-CH_3$$
$$\rightarrow CH_3-CH=CH-CH_3 \rightarrow CH_3-CHBr-CHBr-CH_3$$
$$\rightarrow \underset{\text{butadiene}}{CH_2=CH-CH=CH_2}.$$



*Top and Middle: Courtesy of the Standard Oil of New Jersey*
*Bottom: Courtesy of the B. F. Goodrich Co.*

FIG. 198. *Top:* Butyl Rubber; stretching properties. *Middle:* sample on left is natural rubber, attacked by exposure for a few minutes to ozone; sample on right is Butyl Rubber, unaffected by ozone. *Bottom:* Ameripol being milled like natural rubber.

The double bonds are the reactive portions of the butadiene molecule. At the double bonds, polymerization of the gaseous butadiene to solid rubber occurs; at the double bonds vulcanization with sulfur forms cross-linkages with long chains of isoprene units; at the double bonds oxygen attacks the finally cured, but still greatly unsaturated, rubber. Unfortunately, the double bonds also control elasticity. The industrialist can not therefore protect the rubber against deterioration by oversaturating all of the double bonds, or else the product is rigid and plastic-like. However, by scientific control, two types of rubber are achieved: (*a*) those which, like natural rubber, are unsaturated and can therefore be compounded and vulcanized with it in tire manufacture, and (*b*) those which are more fully saturated. This latter type, which includes Neoprene, Sovprene, and Perbunan, being saturated, are extremely resistant to deterioration by light, heat, oils, ozone, etc.; but they cannot be vulcanized and compounded with natural rubber.

The polymerization of the monomers in Fig. 197 was at one time accomplished by the use of sodium as a catalyst (*i.e.*, Buna, *bu*tadiene + *Na*); but the current method is copolymerization in solution with the rubber monomer and some plastic monomer (*e.g.*, styrene, acronitrile), forming a synthetic latex. Natural latex is the milky liquid obtained from the rubber tree. This latex is coagulated by the addition of acetic acid, by smoke, or by agitation.

Many different ingredients are compounded with rubber, some to cheapen the cost and others for specific purposes. Some of the compounding substances are: litharge (lead monoxide), zinc oxide, magnesium oxide, white lead, clay, barium sulfate, iron oxide, gypsum, carbon-black,

Certain other substances, termed **accelerators**, are added to rubber to shorten the time required for vulcanization, as well as to improve the quality of the product: *e.g.*, aniline, toluidine, etc. **Inhibitors** (anti-oxidants) are added to rubber to prevent oxidation.

**629. Plastics.**—Some plastics soften upon heating, and harden again on cooling; these are **thermoplastic.** Others are sold as molding powders or rods which, when once heated above some critical temperature, become permanently changed so that they cannot be re-molded. These are **thermosetting** plastics.

Another classification of plastics is according to chemical composition or mode of formation: these fall into three categories.

**a. Cellulose plastics.** These have already been discussed. (**535**). Celluloid was one of our earliest plastics (Hyatt, 1868). In 1939 the United States produced 5,230,499 lbs. of nitrocellulose plastics and 5,517,159 lbs. of cellulose acetate molding compositions. Ethyl cellulose is a promising new-comer in this group.

**b. Condensation plastics.** In 1909 Leo Baekeland produced a plastic by heating phenol and formaldehyde together under pressure. Water is split off during reaction, a type of organic change known as **condensation.** Other condensation plastics are formed with urea and formaldehyde. Plastics of this type include Bakelite, Durez, and Catalin. Plywood is often impregnated with phenolic plastics in forming, for example, airplane parts. Approximately 80,000,000 lbs. was produced in the United States in 1939.

**c. Polymerization plastics.** This group of plastics, like synthetic rubber, is formed by polymerization of simple hydrocarbons or their derivatives. A few of the monomers, and the technical names of their polymerized products, are given in Fig. 199. This field of plastics is expanding so rapidly, and has been given such publicity, that it seems unnecessary to elaborate upon it. About 2,000,000 lbs. was produced in 1939.

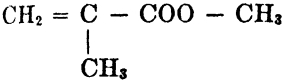
| | |
|---|---|
|  $CH_2 = \underset{\displaystyle \overset{|}{CH_3}}{C} - COO - CH_3$ | methyl methacrylate (*Plexiglas* by Röhm and Haas; *Lucite* by du Pont) |
| $CH_2 = CHCl$ | vinyl chloride (Vinylite by Carbon and Carbide; also contains acetate) |
| $CH_2 = CH - C_6H_5$ | styrene (*Styron* by Dow) |

FIG. 199. Some plastics and the monomers from which they are made.

## QUESTION REVIEW

**Organic chemistry (619).**

1. Distinguish between inorganic and organic chemistry. Between ring and chain compounds.

### I. SATURATED HYDROCARBONS.

**a. Methane series (620).**

2. Write the structural formula for pentane. For decane.

**b. Methane (621).**

3. Show, stating conditions, that methane can undergo either substitution or displacement reactions with chlorine.

**c. Petroleum (622).**

4. How has the legal status of petroleum ownership affected oil technology in the United States?
5. Name five fractions from crude oil, their approximate chemical compositions, and their relative boiling points.
6. Explain: wildcatting, cracking, use of seismographs, "Christmas tree," asphalt base, polymerization, petroleum gases, mercaptans, alkylation, a knock rating of 75, isooctane, the cause of engine knock.

**d. Synthetic gasoline (623).**

7. Outline the processes, and state the military advantages of the Fischer-Tropsch process over the Bergius process.

**e. Other synthetic fuels (624).**

8. State an important fact about each of the following: (*a*) source of power alcohol (*b*) value of benzene (*c*) use of charcoal in automobiles.

**f. Products from petroleum (625).**

9. Describe uses for three substances which only recently have been synthesized from petroleum products.

### II. UNSATURATED HYDROCARBONS.

**a. Ethylene (626).**

10. Write an equation, using structural formulas, showing the dehydration of propyl alcohol ($C_3H_7OH$), and subsequent treatment of the product with bromine.

**b. Acetylene (627).**

11. Write equations, in steps, showing the production of acetylene from coal, limestone and water.

**c. Rubber (628).**

12. Write the structural formulas for two rubber monomers, naming them.
13. What role has each of the following played in rubber technology: sodium, limestone, potatoes, petroleum, hydrogen chloride, double bonds, polymerization, accelerators, inhibitors?
14. Why does over-vulcanization produce hard rubber?

**d. Plastics (629).**

15. Plastics may be classified according to what two physical properties? Into what three classes as regards chemical composition?
16. Tabulate the quantities of various plastics produced in the United States.

**Reading References:** Articles in the Appendix:

*General:* 119, 153, 226, 255 and 409.

*Paint:* 16, 46, 125 and 226.

*Petroleum:* 134, 136, 143, 147, 226, 231, 233, 245, 342 and 343.

*Plastics:* 129, 152, 226, 234, 249, 255, 326, 329 and 338.

*Rubber:* 34, 63, 144, 149, 226, 251, 252, 306, 326, 339, 343, 406, 411, 416 and 417.

*Strategic materials:* 133, 140, 142, 145, 151, 252, 326, 340, 345, 411, 412 and 416.

# CHAPTER XLII

# CHAIN COMPOUNDS

## PART II. ALCOHOLS. ACIDS. ESTERS

**630. Organic Radicals.**—There are many groups of atoms containing carbon which pass unaltered from compound to compound. Such groups usually have a valence of one and are called *organic radicals*. The following radicals and compounds containing them may serve as illustrations:

| *Radical* | | *Chloride* | | *Alcohol* | |
|---|---|---|---|---|---|
| $CH_3$, | Methyl | $CH_3Cl$, | Methyl chloride | $CH_3OH$, | Methyl alcohol |
| $C_2H_5$ | Ethyl | $C_2H_5Cl$, | Ethyl chloride | $C_2H_5OH$, | Ethyl alcohol |
| $C_3H_7$ | Propyl | $C_3H_7Cl$, | Propyl chloride | $C_3H_7OH$, | Propyl alcohol |

The radical $C_nH_{2n+1}$, known as an **alkyl radical**, may be derived from the corresponding hydrocarbon by withdrawing one atom of hydrogen.

### ALCOHOLS

**631. Definition.**—An alcohol is an hydroxide of an alkyl radical. Those containing one hydroxyl group have the general formula, $C_nH_{2n+1}OH$ or ROH. We may regard them as being derived from the paraffins by the substitution of the hydroxyl group for one atom of hydrogen:

$$\text{Methane, } CH_3H \rightarrow CH_3OH\text{, Methyl alcohol,}$$
$$\text{Ethane, } C_2H_5H \rightarrow C_2H_5OH\text{, Ethyl alcohol.}$$

Alcohols are somewhat analogous to bases, but they do not ionize in water to furnish hydroxide ion.

Alcohols of the series $C_nH_{2n+1}OH$ can be prepared by the action of moist silver oxide upon alkyl halides:

$$C_nH_{2n+1}I + AgOH \rightarrow C_nH_{2n+1}OH + AgI \downarrow.$$

**Glycerine or glycerol**, $C_3H_5(OH)_3$, is an alcohol belonging to another series; it is called a trihydric alcohol.

**632. Methanol, $CH_3OH$.**—Methanol, also called *methyl alcohol, wood alcohol,* or *wood spirits,* is obtained from water gas:

$$CO + 2H_2 \xrightarrow[\text{catalyst}]{ZnO + Cr_2O_3} CH_3OH.$$

This is a "by-product process" for removing CO from producer gas in the Haber Process (**514**).

As late as 1924 the wood-distillation industry flourished. The pyroligneous liquor (or "acid") obtained during the destructive distillation of wood contains methanol, acetic acid, acetone, etc.; hence the name "wood alcohol." Synthetic methanol developed in Germany in 1924, soon annihilated the wood-distillation industry, and tumbled the price of methanol from 75¢ to 15¢ a gallon.

Pure methyl alcohol is a colorless liquid with a specific gravity of 0.796 at 20°; it boils at about 66°, possesses a wine-like odor and a burning taste, and mixes with water in all proportions. The alcohol burns with a pale, non-luminous flame, with the production of much heat:

$$2CH_4O + 3O_2 \rightarrow 2CO_2 + 4H_2O + 341{,}800 \text{ cals.}$$

Methanol is quite poisonous when taken in concentrated form, and has the property of affecting the optic nerve, producing blindness. During prohibition times many cases of blindness were reported of victims who had drunk wood alcohol instead of grain alcohol.

Methyl alcohol is used as a solvent for shellacs and resins, in manufacturing varnishes and dyes, and as an anti-freeze for automobile radiators (*e.g.*, "Zerone").

**633. Ethanol, $C_2H_5OH$.**—Ethyl alcohol is also called *grain alcohol* and *spirit of wine;* it has been known since ancient times, for it is contained in all fermented liquors.

**a. Fermentation of sugars.** Alcohol can be prepared by the fermentation of sugars and molasses. By placing an aqueous solution of glucose (5 to 10 per cent) in a flask and adding a few small pieces of brewer's yeast and setting the flask in a warm place (20° to 30°), fermentation soon sets in, alcohol and carbon dioxide being produced:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2.$$

By fitting the flask with a cork and a delivery tube the formation of carbon dioxide can be proved by passing the evolved gas through limewater. When the fermentation is at an end, the alcohol may be concentrated by fractional distillation. If lime be added to the distillate, water is taken up, and by distilling a second time a more concentrated product is obtained.

The enormous potential supply of "power alcohol" (*i.e.*, ethanol as automobile fuel) has already been discussed (**624**).

**b. Fermentation of starch.** Alcohol is also manufactured on a large scale from grain, potatoes, and other starch-containing materials.

The raw material is reduced to a pulp or paste, a little malt (from barley or other grain) added, and the starch fermented to maltose (a sugar) and dextrin. Yeast is now added, and the solution kept until the alcoholic fermentation is at an end. Maltase (present in yeast) hydrolyzes the maltose to glucose, and zymase ferments it. The weak solution of alcohol obtained by fermentation is subjected to fractional distillation.

Alcohol is used extensively as a solvent, a fuel, and for the production of ethylene. Denatured alcohol is ethyl alcohol to which gasoline, pyridine, methanol, benzene, etc., are added to make it unfit for use as a beverage.

Pure ethyl alcohol is a colorless liquid having a specific gravity of 0.806 at 0° and of 0.793 at 15°. Its boiling point is 78.3°, it freezes at −112°, and mixes with water in all proportions. It burns, forming carbon dioxide and water.

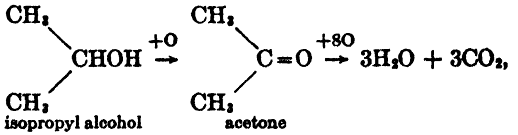
When a water solution of ethanol is heated, a constant-boiling mixture (144) containing 95 per cent ethanol and 5 per cent water is formed. This is the ethanol usually found about the laboratory. For much organic work, however, **absolute alcohol** is required; this is manufactured industrially by a special distilling technique in which benzene is added during the distillation.

Alcohol is classified on the proof gallon, which contains 50 per cent water *i.e.*, absolute alcohol is 200 proof, while 95 per cent alcohol is 190 proof. Whiskey, rum, brandy and gin are slightly under 100 proof. Wines (10–20%) and beers (2–6%) are usually expressed in terms of the percentage of alcohol by volume.

**634. Aldehydes and Ketones.**—The oxidation products of two different types of alcohols are shown below:

$$\underset{\text{methanol}}{CH_3OH} \xrightarrow{+O} \underset{\text{formaldehyde}}{HCHO} \xrightarrow{+O} \underset{\text{formic acid}}{HCOOH} \xrightarrow{+O} H_2O + CO_2.$$

**Formaldehyde,** HCHO, is obtained by passing a mixture of the vapor of methyl alcohol and air over a hot platinum or copper spiral. It is a colorless, pungent gas, and very soluble in water. The 40 per cent aqueous solution is known as "formalin." Formaldehyde is used as a disinfectant, for preserving anatomical specimens, for hardening gelatins (*e.g.*, in the manufacture of leather), and for the production of *bakelite* (629). It belongs to a class of organic compounds known as **aldehydes.**



**Acetone,** $(CH_3)_2CO$ is the most important member of a class of compounds known as **ketones.** It is produced on a large scale by fermenting carefully sterilized corn or potato-starch with spores of Weizmann bacteria; butyl alcohol and acetone are obtained. The alcohol is used in Russia for making butadiene rubber (628); the acetone is an excellent organic solvent.

### ORGANIC ACIDS

**635. The Fatty Acids.**—The acids of this homologous series owe their name to the fact that some of the members are constituents of animal fats and animal and vegetable oils. The general formula is $C_nH_{2n}O_2$, or $C_nH_{2n+1}COOH$. The radical (COOH) is called the **carboxyl group** and is characteristic of organic acids. Representing univalent organic radicals as R, the general formula for an acid, and the manner in which it ionizes is

$$RCOOH \rightarrow RCOO^- + H^+$$

*e.g.*,

$$\underset{\text{acetic acid}}{CH_3COOH} \rightarrow CH_3COO^- + H^+.$$

As is indicated in the foregoing section, organic acids are obtained as oxidation products of certain alcohols: *i.e.*,

$$CH_3OH \rightarrow HCOOH; \quad \text{and} \quad CH_3-CH_2-OH \rightarrow CH_3COOH.$$

**Formic acid, HCOOH,** is the first member of the fatty series; it occurs in nettles and in the sting of bees and ants (Latin, *formicae*).

**Higher fatty acids** contain many $CH_2$ groups in long chains, *e.g.*, palmitic acid, $C_{15}H_{31}COO-H$, and stearic acid, $C_{17}H_{35}COO-H$; they are found in animal fats.

**636. Acetic Acid, $CH_3COOH$.**—Approximately 100,000 tons of acetic acid is produced each year by the catalytic oxidation of acetaldehyde:

$$CaCO_3 + C \longrightarrow CaC_2 \xrightarrow{+H_2O} C_2H_2 \xrightarrow[\substack{HgSO_4\\ \text{catalyst}}]{+H_2O} CH_3CHO \xrightarrow{+O} CH_3COOH$$

The acid flows out of the reaction chamber like soft ice.

Acetic acid is also obtained (as acetic anhydride) from the distillation of wood. In this form (acetic anhydride, $(CH_3C)_2O$), it is used in manufacturing cellulose acetate plastics (**629**).

Pure acetic acid (hydrogen acetate) is a white, colorless, crystalline solid, which melts at 16.5° and boils at 118°; it has a penetrating smell and a sour taste. Because of the ice-like appearance of the frozen material, it is called glacial acetic acid. The compound mixes with water in all proportions, and its aqueous solution is a weak acid. See page 191.

**Vinegar.** When fruit juices (cider, weak wine, etc.) or beers are left exposed to air, they soon become sour, because of oxidation of alcohol to acetic acid:

$$\underset{\text{Alcohol}}{CH_3CH_2OH} + O_2 \rightarrow H_2O + \underset{\text{Acetic acid}}{CH_3COOH}.$$

This oxidation is brought about by the agency of "mother of vinegar," or acetous ferment (*Mycoderma aceti*), a low order of plant. Vinegar, then, is essentially a dilute solution of acetic acid; it also contains coloring matter and other substances.

## ESTERS. SOAP

**637. Esters.**—These compounds are formed by the interaction of an alcohol and an acid. This is comparable with the reaction in inorganic chemistry between an hydroxide and an acid:

*inorganic:*

$$\overset{\text{hydroxide}}{Na-OH} + \overset{\text{acid}}{H-Cl} \rightarrow \overset{\text{water}}{HOH} + \overset{\text{salt}}{NaCl}$$

*organic:*

$$\underset{\text{ethanol}}{\overset{\text{alcohol}}{C_2H_5-OH}} + \underset{\text{acetic acid}}{\overset{\text{acid}}{CH_3COO-H}} \rightleftarrows \overset{\text{water}}{HOH} + \underset{\text{ethyl acetate}}{\overset{\text{ester}}{CH_3COO-C_2H_5}}$$

The formation of an ester is known as **esterification**. It is favored by adding concentrated sulfuric acid which, by removing water, drives the reaction to the right (why?). The reverse reaction, the formation of alcohol and acid from an ester, is known as **hydrolysis** (write an inorganic hydrolysis reaction). The addition of water hydrolyzes an ester, driving the above reaction to the left. Unlike inorganic salts, **esters do not ionize.**

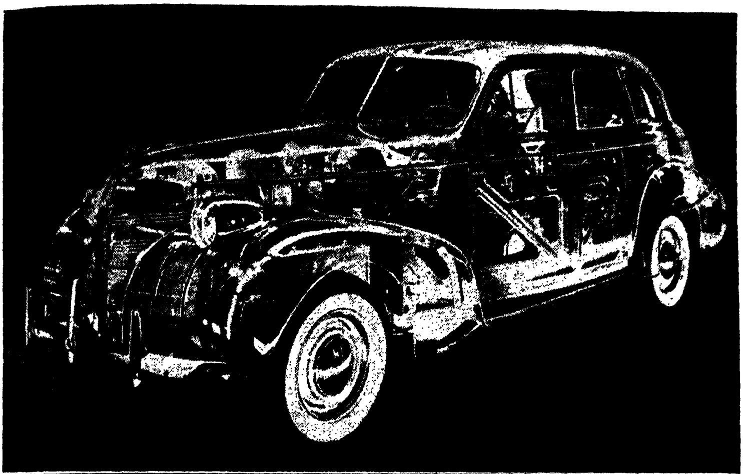
**Fruit odors.** *Ethyl acetate* is an example. It is formed in apples; for ethyl alcohol and acetic acid, formed from the fermentation of the sugar in apples would esterify to ethyl acetate. *Amyl acetate* is banana-oil; the odor of bananas emanating from a newly-painted radiator attests the use of esters as a solvent in lacquers. *Ethyl butyrate* is the odor of pineapple. *Vanilla* is an ester now produced synthetically as well as extracted from the vanilla bean.

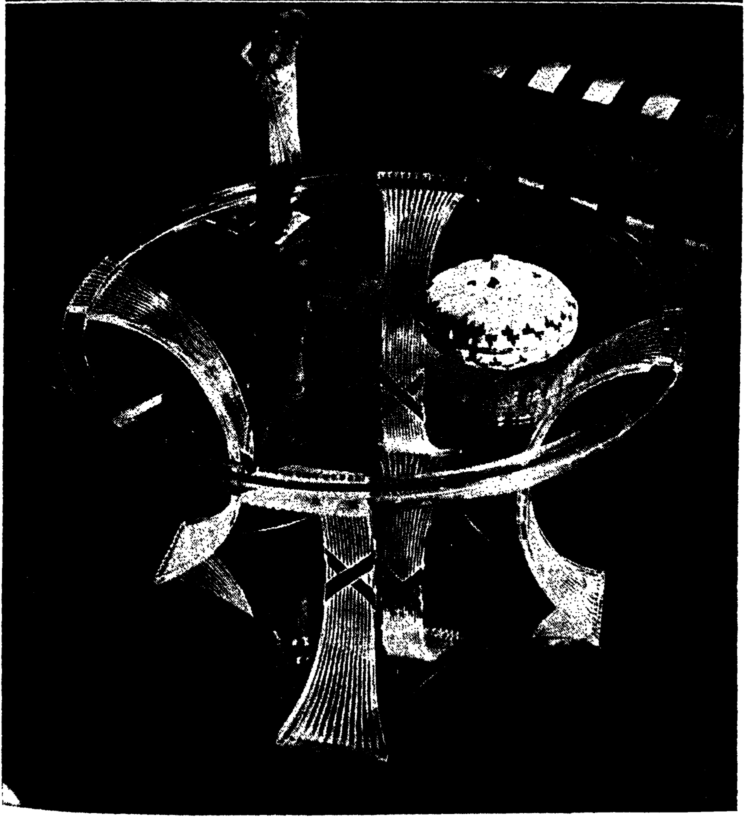
**Perfumes.** Costly perfumes contain as many as a hundred different esters skillfully blended. When Catherine de Medici came to Paris as the bride of Henry the Second she brought with her from Corsica a retinue of court chemists, professional blenders of perfumes.

**Cellulose esters.** The hydroxyl radicals in cellulose may be substituted to give the important esters, *cellulose acetate* and

*Courtesy of Röhm and Haas Company, Inc.*
*Photo by Louis Werner*

FIG. 200. Plexiglas. *Top:* crystal-clear methyl methacrylate plastic, formed along Fisher Body lines, makes the construction of the Pontiac visible for display purposes. *Bottom:* Plexiglas pedestal, designed by Lorin Jackson.





*cellulose nitrate.* The varied uses of these as plastics, lacquers, textile coatings, moving picture film, explosives and so forth has already been described (**535**). *Glyceryl trinitrate* is another inorganic-organic ester (**534**).

**Fats.** Fats are glyceride esters of the higher fatty acids:

| | | |
|---|---|---|
| $(C_{15}H_{31}COO)_3C_3H_5$ | glyceryl palmitate | (solid), |
| $(C_{17}H_{35}COO)_3C_3H_5$ | glyceryl stearate | (solid), |
| $(C_{17}H_{33}COO)_3C_3H_5$ | glyceryl oleate | (liquid), |
| $(C_{31}H_{17}COO)_3C_3H_5$ | glyceryl butyrate | (solid). |

*Tallow* contains chiefly the stearin and palmitin esters; and *lard*, which is a soft fat, contains considerable quantities of the olein ester. *Butter* contains those same esters together with butyrin ester. *Oleomargarine* is an artificial butter produced by churning the softer fats from cattle or hogs with a little oil (*e.g.*, cottonseed) and milk. When properly made, it is wholesome.

**638. Hydrogenation of Oils.**—Liquid oils (*e.g.*, cottonseed, fish, whale, soy-bean oil, etc.) contain unsaturated glyceryl esters, such as glyceryl linoleate and glyceryl oleate. By hydrogenating these unsaturated compounds, solid fat is obtained:

$$\underset{\text{liquid oil}}{(C_{17}H_{33}COO)_3C_3H_5} + 3H_2 \rightarrow \underset{\text{solid fat}}{(C_{17}H_{35}COO)_3C_3H_5}.$$

This is the process for making solid butter substitutes, such as Crisco, from cottonseed oil. The importance of the process is emphasized by the statement that in 1940 the United States hydrogenated 500,000,000 pounds of soy-bean oil to make a solid lard.

Although chemists appointed by Napoleon to find a substitute for butter realized that there was a relation between oils and fats, it was not until 1912 that the French chemist Sabatier perfected the process of high pressure hydrogenation of oils over nickel or nickel oxide catalysts.

These same oils are hydrogenated in the manufacture of *soap from cottonseed oil.* The unsaturated soap is soft and turns rancid; saturation makes it hard and resistant to deterioration, just as saturation of double bonds in synthetic rubber increases its resistance to oxidation (**628**).

**639. Soap.**—Soaps are metallic salts of fatty acids. In practice, soaps are confined to sodium and potassium salts of fatty acids containing ten or more carbon atoms. Sodium soaps are hard, while potassium soaps are soft.

In manufacture, the soap is heated with lye:

$$\underset{\text{glyceryl stearate}}{(C_{17}H_{35}COO)_3C_3H_5} + \underset{\text{lye}}{3NaOH} \rightarrow \underset{\text{soap}}{3C_{17}H_{35}COO - Na} + \underset{\text{glycerine}}{C_3H_5(OH)_3}.$$

The fat is hydrolyzed to form a fatty acid, which then combines with lye to form the sodium salt. The process is called **saponification** (Latin *sapo*, soap, *facere*, to make).

The "stock," or mixture of glycerides, is brought to the top of a huge kettle by means of a pipe. Lye and water are also brought to the kettle until it is filled. A single kettle will hold "stock" enough to yield hundreds of thousands of pounds of soap (Fig. 201). Steam is blown in at the bottom of the kettle and its contents are thoroughly agitated and boiled until a pasty mass of soap is obtained. In the next operation common salt is added, which causes the globules of glycerine and water to sink to the bottom of the kettle and the clear soap curd to form a layer on top (why?). The water and glycerine are withdrawn from the bottom.

*Courtesy of Swift and Company*

FIG. 201. Top of a soap kettle.

The soap curd, after purification, is pumped into large stirring bowls, or "crutchers," where it is stirred until smooth. Coloring matter, perfumes, medicinals, fillers, etc., may be added. To produce floating soap, air is beaten into it. The soap is next emptied into "frames," which are similar to boxes, but with detachable sides, where it is allowed to cool. The large blocks of soap are finally cut by machinery into small cakes, dried, stamped, and wrapped.

The **Twitchell process** is used on low-grade fats or greases. The fat is rendered partially miscible in water by adding sulfuric acid, and the mixture is boiled. After the free fatty acid is formed by hydrolysis (write equation) it is treated with $Na_2CO_3$.

Years ago in our own country, soap-making was one of the household arts or industries. Soap was produced by dissolving the "potash" out of wood ashes, the solution being known as "lye." The fat, or "soap-grease," saved by the housewife was heated in iron kettles with potash lye, *soft soap* being obtained.

**Soapless soaps.** Since 1930 a new type of **detergent**, as it is called, has appeared. One source is coconut oil (glyceryl laurate), which is changed as follows:

$$\underset{\textit{coconut oil}}{(C_{11}H_{23}COO)_3C_3H_5} \rightarrow \underset{\text{ethyl laurate}}{C_{11}H_{23}COO-C_2H_5} \xrightarrow{+H_2} \underset{\text{lauryl alcohol}}{C_{11}H_{23}-CH_2-OH}$$

$$\xrightarrow{+H_2SO_4} \underset{\text{lauryl sulfonic acid}}{C_{11}H_{23}CH_2O-SO_3H} \xrightarrow{NaOH} \underset{\substack{\text{sodium lauryl sulfonate} \\ \textit{soapless soap}}}{C_{11}H_{23}CH_2O-SO_3-Na.}$$

These detergents form a rich lather with sea-water, for their calcium and magnesium salts are soluble, unlike those of ordinary soap. For the same reason, no "ring in the bath-tub" is formed. "Gardinol," "Dreft" and "Drene" are examples of this very modern product of chemical industry.

## QUESTION REVIEW

**Organic radicals (630).**

1. Write the following: butyl radical, heptyl chloride, octyl alcohol.

I. ALCOHOLS.

**a. Definition (631).**

**b. Methanol, $CH_3OH$ (632).**

2. Give the equation for the reaction which led to the downfall of the wood distillation industry. What is its connection with the Haber process?

**c. Ethanol, $C_2H_5OH$ (633).**

3. Give an equation showing how India obtains its power alcohol.
4. What part does each of the following play in alcohol chemistry: grain, malt, anti-freeze, denaturant, absolute alcohol, 190 proof.

**(Aldehydes and ketones, 634).**

5. Describe the industrial importance of formaldehyde. Of acetone.

II. ORGANIC ACIDS.

**a. The fatty acids (635).**

6. Give equations showing the oxidation products of butyl alcohol. Of isobutyl alcohol.
7. Is palmitic acid saturated or unsaturated?

**b. Acetic acid (636).**

8. Outline the production of vinegar. Of acetic acid.

III. ESTERS AND SOAP.

**a. Esters (637).**

9. Give one example each of four different types of industrial esters.
10. Write an equation illustrating hydrolysis. Illustrating esterification.
11. Olein is liquid. In what way is it chemically different from the other three fats listed in this section?

**b. Hydrogenation of oils (638).**

12. Why do oils turn rancid less easily *after* they have been hydrogenated?
13. How many tons of hydrogen was required to hydrogenate soy-bean oil in the United States in 1940?

**c. Soap. Soapless soaps (639).**

14. Write an equation illustrating saponification to form a *soft* soap.
15. What property of soapless soaps enables it to lather with seawater?
16. In a general way show that the formula for soapless soaps is radically different from that for ordinary soaps.

**Reading References:** Articles in the Appendix:

*Alcohols:* 102, 119, 138, 245, 338, 406, 411, 416 and 429.

*Cellulose esters:* 110, 125, 311 and 333.

*General:* 1, 102, 253, 306, 307 and 338.

*Strategic materials:* 133, 140, 142, 145, 151, 252, 326, 340, 345, 411 412 and 416.

# CHAPTER XLIII

# RING COMPOUNDS

**640. The Benzene Ring.**—One class of ring or cyclic compounds is derived from **benzene, $C_6H_6$.** They are called the **aromatic compounds.**

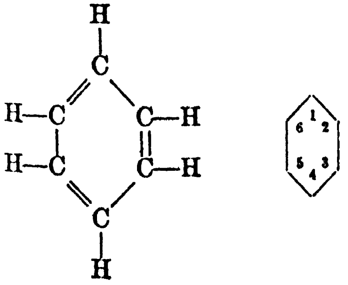
Benzene was discovered by Faraday in 1825. It is a colorless, mobile liquid having an aromatic odor. It boils at 80°, its specific gravity is 0.88 at 20°, and it is insoluble in water. Benzene is a solvent for fats, resins, phosphorus, etc. It burns with a luminous, smoky flame.

In 1866 Kekule proposed the ring structure for benzene which is accepted today.

Kekule wrote: "I was sitting, writing at my text-book; but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire and dozed. Again the atoms were gamboling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of this kind, could now distinguish larger structures, of manifold conformation: long rows, sometimes more closely fitted together; all twining and twisting in snake-like motion. But look! what was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightening I awoke; and this time also *I spent the rest of the night in working out the consequences of the hypothesis.*"

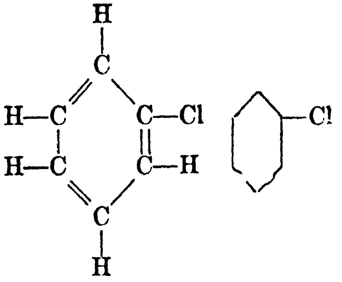
Kekule's ring structure has been substantiated in a number of ways:

*a. Every carbon has four bonds.* This is shown in Fig. 202. Very few configurations can be written with 6C and 6H to give



benzene numbered

Fig. 202. Benzene.



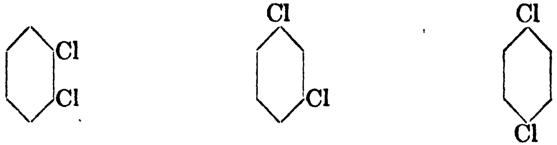
mono-chloro-benzene usual notation

Fig. 203. Mono-chloro-benzene.

carbon a valence of four. Of the possible configurations, only the ring structure satisfies fact (b):

*b. There is only one mono-chloro-benzene, $C_6H_5Cl$, known.* This is consistent with the ring structure shown in Fig. 203. Since the ring is a hexagon, it does not matter which hydrogen is replaced by chlorine; in every instance the same mono-chloro-benzene is obtained. The chemist usually abbreviates the ring as shown in the last figure.

*c. There are only three di-chloro-benzenes, $C_6H_4Cl_2$, known.* This, also, is in accord with the Kekule formula. The positions of the two chlorine atoms are designated as ortho, meta and para respectively, Fig. 204. Regardless of which carbon atoms the chlorine atoms are attached to, the various configurations all may be identified as one of three types, *e.g.*, ortho, meta, or para dichloro-benzene.



ortho di-chloro-benzene
b.p. 180°
m.p. − 17.5°

meta di-chloro-benzene
b.p. 172°
m.p. − 24.8°

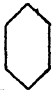
para di-chloro-benzene
b.p. 173.4°
m.p. +53°

FIG. 204.

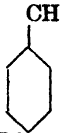
*Question.* How many tri-chloro-benzene derivatives are there?

*d.* Accepted for many years, the arrangement of the carbon atoms in this form has been recently substantiated by X-ray data and by dielectric constant measurements, the latter demonstrating that the benzene molecule is perfectly symmetrical as regards charge. This research also shows that the benzene ring is not flat but puckered, the carbon atoms projecting alternately above and below the medial plane.

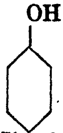
**641. Other Ring Compounds.**—There are many important derivatives of benzene. Some of these are shown below:



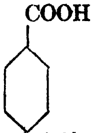
**Benzene**
$C_6H_6$



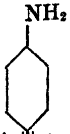
**Toluene**
$C_6H_5—CH_3$



**Phenol**
$C_6H_5—OH$



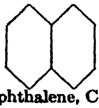
**Benzoic Acid**
$C_6H_5—COOH$



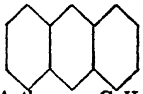
**Aniline**
$C_6H_5—NH_2$

*Courtesy of the Scranton Chamber of Commerce*

Other compounds contain several benzene rings:



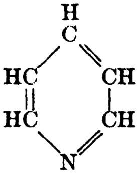
Naphthalene, $C_{10}H_8$



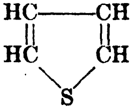
Anthracene, $C_{14}H_{10}$

Naphthalene is a white crystalline compound melting at 80° and boiling at 218°. It is sold in the form of "moth-balls." Naphthalene is used largely in the manufacture of dyes, about 25,000 tons being produced annually in America.

Still other compounds do not belong to the benzene series; these form rings containing a variety of elements:



pyridine



thiophene

Finally, many of the complex materials such as carbohydrates, plastics, proteins, etc., contain "rings" of carbon, oxygen, nitrogen, etc., within their giant molecules.

**642. Products from Coal.**—When a ton of coal is destructively distilled it yields, on the average, 12,000 cu. ft. of hydrogen and methane, with smaller quantities of carbon monoxide and unsaturated hydrocarbons. Also produced are 1,200 to 1,400 pounds of coke, about 120 pounds of tar, and ammonia liquor enough to manufacture from 7 to 25 pounds of ammonium sulfate.

### DEMONSTRATION 161. DISTILLATION OF COAL

Materials: Set-up in Fig. 205.

**Coal tar.** The tar is a complex mixture containing hundreds of aromatic compounds; it owes its black color to suspended particles of carbon. Present in the coal tar is 5 to 10 per cent naphthalene and about 1½ per cent of a mixture of benzene and toluene. Phenol (carbolic acid, $C_6H_5OH$) is a principal acidic component. Basic components are not present in large amounts the chief one being pyridine ($C_5H_5N$), a liquid with a disagreeable odor; it has been used for denaturing alcohol.

Tar, like petroleum, is separated into components by **fractional distillation,** which is conducted in large iron stills or retorts, the vapors being condensed in long metallic worms immersed in cold

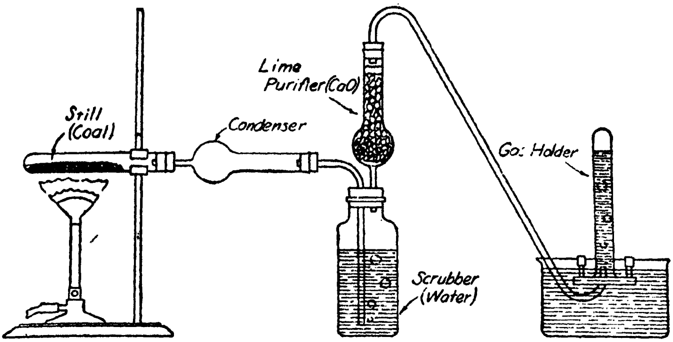


FIG. 205. Distillation of coal in the laboratory (Demonstration 161).

water. The resulting liquid distillate is collected in four fractions, as shown below.

TABLE 122. FRACTIONS FROM COAL TAR

| Fraction | Temperature | Density |
|---|---|---|
| I. Light Oil, or Crude Naphtha | 80°–170° | 0.910–0.950 |
| II. Middle Oil, or Carbolic Oil | 170°–230° | 1.01 |
| III. Heavy Oil, or Creosote Oil | 230°–270° | 1.04 |
| IV. Anthracene Oil, or Green Oil | Above 270° | 1.10 |
| V. Pitch | residue | — |

The **light oil** is separated into its components by further fractionation and then purified, partly by chemical means. The principal substances derived therefrom are benzene and its homologues, toluene and xylene:

| | |
|---|---|
| Benzene | $C_6H_6$ |
| Toluene, or Methyl Benzene | $C_7H_8$, or $C_6H_5CH_3$ |
| Xylene, or Dimethyl Benzene | $C_8H_{10}$, or $C_6H_4(CH_3)_2$. |

These belong to the homologous series having the general formula $C_nH_{2n-6}$.

It should be added that much benzene and toluene are obtained by scrubbing the gases from the retorts, when coal is carbonized, in a spray of heavy oil. The compounds may be recovered from solution by distillation.

**Coal Gas.**—Large quantities of coal gas are produced by the destructive distillation of coal at high temperatures. *Coke, tar,* and *ammonia* are the *by-products.* Bituminous coal is heated to high temperatures in retorts, from which a pipe leads to the *hydraulic main,* where tar and water are condensed. The excess of tar flows into a *tar pit.* The hot gases and vapors are next passed through a series of pipes called *condensers,* to condense more tar and to cool the gas for further purification. The liquids collected in the tar pit separate

TABLE 123. PRODUCTS FROM DISTILLATION OF COAL
(U. S. A. for 1939)

- 63,513,684 tons of COAL
  - 40,212,242 metric tons of COKE
  - 675,143,201 million cubic feet of COAL GAS
  - 676,802 tons of AMMONIA (as sulfate)
  - 554,406,216 gallons of TAR
    - LIGHT OIL: motor fuel. Toluene, solvent naphtha, xylene 139,805,191 gallons
    - NAPTHALENE 24,230 tons
    - TAR
      - creosote: 19,455,849 gallons
      - pitch: 215,414 tons
    - PHENOL and derivatives 388,339 gallons

into two layers—the lower is coal-tar and the upper is gas liquor (an aqueous solution of ammonia and ammonium compounds). The cooled gas is passed from the condensers to the *scrubber*, where ammonia is dissolved by water.

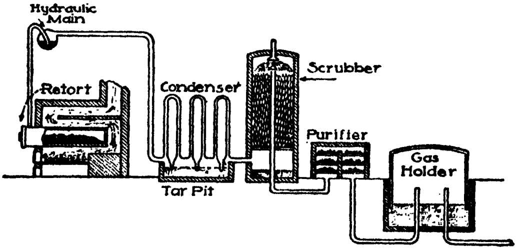


FIG. 206. Manufacture of coal gas.

The gas passes from the scrubber to the *purifiers*, where hydrogen sulfide is taken out by hydrated ferric oxide or lime. From the purifiers the gas passes to the *holder*, where it is stored over water and piped to the consumer.

## COAL-TAR PRODUCTS

During the latter part of the nineteenth century, a vast industry for synthesizing chemicals from coal-tar derivatives arose. Some of these varied products will now be described.

**643. Dyes.**—In 1856 a young man seventeen years of age, later to be known as Sir William Perkin, treated aniline with potassium dichromate, hoping to oxidize it to quinine. Instead of producing quinine, he synthesized the first of the basic coal-tar colors, and named it "mauve." This complex dye was the beginning of the coal-tar dye industry. Perkin not only discovered the first of these aniline dyes; he also pushed them into commercial production. Today from *coal tar*, ten "crudes" (benzene, toluene, naphthalene, anthracene, carbolic acid, etc.) are obtained. From these about a thousand "intermediates" are produced, and from the intermediates, thousands of dyes.

**Alizarin** was one of the earliest important dyes to fall under the power of the synthetic chemist. The madder root, from the fields of France and along the Mediterranean Basin, supplied this important dye, known as "Turkey Red" and used for centuries. It soon became evident that alizarin was related structurally to anthracene (Fig. 207); and in the race which ensued, Germany beat England by a single day for this dye supremacy (Graebe and Liebermann filed patent application on June 25, 1869, Perkin filed his patent June 26, 1869).

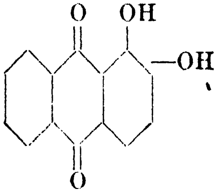


FIG. 207. Alizarin.

Professor H. W. Close of Beirut relates how it was customary to plant an acre of madder in Syria whenever a boy-baby was born, so that by the time he had grown to conscription age the income from the madder field would hire an alternate for him, a custom which ceased with the rise of synthetic alizarin.

**Indigo** ($C_{16}H_{10}N_2O_2$) is one of the oldest and fastest of dyes.

Certain tropical plants contain a glucoside known as *indican*, which yields **indigo blue**, or **indigotin**. When the leaves and stems of the indigo plant are steeped in lukewarm water and allowed to ferment, a yellow liquid is obtained which contains **indigo white** ($C_{16}H_{12}N_2O_2$). When the solution of indigo white is violently agitated in the presence of air, the indigo white is transformed into insoluble indigo blue. As late as 1897 India devoted about a million acres to the cultivation of the indigo plant. Then von Baeyer established its structure. It was at once evident that the material might be synthesized industrially. The Badische company spent 28 million marks attempting to bring about the most troublesome step in the synthesis, the conversion of naphthalene to phthalic acid (Fig. 208). After bitter failure, a clumsy laboratory boy dropped and broke a thermometer in a batch of the molten naphthalene. Lo! straightway the stuff seethed and boiled, and forthwith turned into the desired phthalic acid. Mercury was the catalyst.

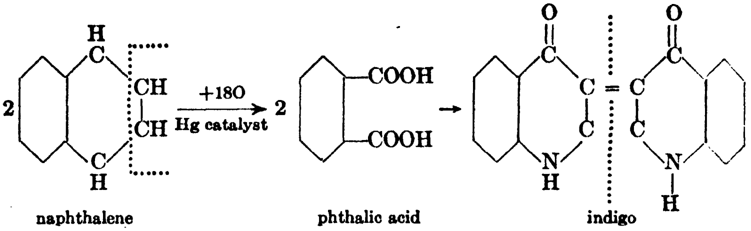


FIG. 208. Synthesis of Indigo.

Germany conquered the indigo market. The income in India from this valuable dyestuff speedily dropped from $20,000,000 a year to $300,000; and during the war of 1914–18 the Scotch had to smuggle dyes to color their kilts. Today Swiss and American dyes rival those of Germany.

**Dyeing.** Some dyes fix themselves firmly to a particular fabric (*e.g.*, *picric acid* on silk and wool; or *congo-red* on wool and cotton). These are called **substantive dyestuffs.** A second type of dyes (**adjective dyestuffs**) require an intermediate, called a **mordant** (Latin, *mordere*, to bite), to fix and fully develop the color (*e.g.*, $Al(OH)_3$ is used to mordant Turkey Red).

**644. Drugs.**—Many drugs are prepared from coal-tar derivatives. A few familiar compounds are shown in Fig. 209.

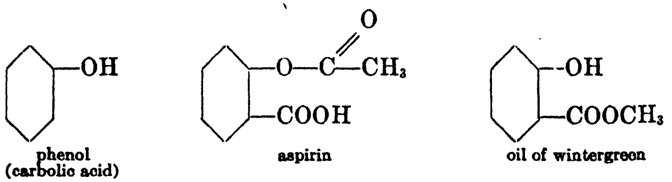
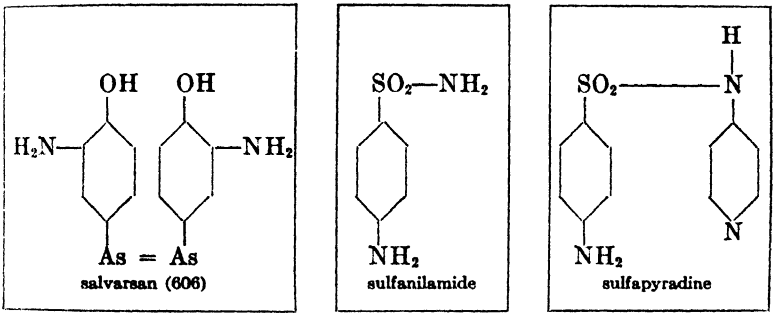


FIG. 209. Some Common Drugs.

During the last two decades of the nineteenth century Paul Ehrlich, working in Koch's laboratory, labored in an attempt to find compounds which specifically dye trypanosomes injected into mice, but which do not harm the mice. His partial successes won for him a new laboratory at Frankfort, where numerous aromatic compounds containing arsenic were tested. Six hundred six compounds were prepared before complete success was pronounced. And then, Ehrlich read Schaudinn's discovery that trypanosomes were related to the spirochetes which cause syphilis. **Salvarsan,** compound 606, was immediately tried on the latter germ, and found to kill it speedily. A direct result of this pioneer work resulted in twelve million doses of arsenical drugs being administered in the United States in 1940.

Indirectly these researches of Ehrlich paved the way for chemotherapy (chemical cure). The important work of G. Domagk (1932–1942) on specific dyes related to prontosil (sulfanilamide etc.) reflect the continuing principle of chemotherapy, as initiated by Ehrlich. Fig. 210 gives the structures of some of these important aromatic compounds.



salvarsan (606) sulfanilamide sulfapyradine

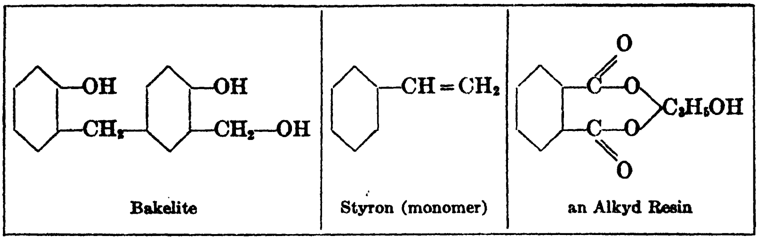
FIG. 210. Drugs in Chemotherapy.

**645. Explosives.—Picric acid** and **tri-nitro-toluene** have already been discussed (536).

Picric (Greek, meaning *bitter*) acid, or **trinitrophenol** ($C_6H_2(NO_2)_3OH$), was discovered by J. A. Glauber in the seventeenth century. He obtained it by treating wood with nitric acid. In 1771 Woulfe accidentally obtained picric acid by the action of nitric acid upon indigo. Picric acid has long been produced by the nitration of phenol, a derivative of coal tar. It is a yellow solid, is fairly soluble in hot water, and has an intensely bitter taste. Sprengel (1871) discovered that this acid may be detonated by fulminate of mercury. It is a yellow dye for silk and wool. Picric acid is 2-4-6-trinitrophenol. (Write its formula.)

**646. Plastics.**—The use of phenol in forming the Bakelite-type plastics has already been described. Styrene is another aromatic compound which forms plastics (629). Still a third type is known as **alkyd resins.**

Structures for these are given below.



Bakelite

Styron (monomer)

an Alkyd Resin

FIG. 211. Some Aromatic Plastics.

DEMONSTRATION 162. MAKING AN AROMATIC PLASTIC

Materials: Four 400-cc. beakers; 100 cc. saturated aniline hydrochloride in water; 100 cc. formalin (40 per cent formaldehyde); stirring rod, mortar and pestle, conc. $NH_4OH$.

Pour formalin into aniline hydrochloride and immediately set the glass rod in the center. A hard mass is formed. Half of this placed in conc. ammonium hydroxide turns white and bone-hard. The other half, placed in water, slowly turns black.

— — — — — — — — —

And so we come to the end of a tale of the strangest combination of compounds man has ever conceived; synthetic dyes which rival nature's prettiest colors, medicines far more potent than herbs and natural concoctions, violent explosives, and a host of plastics. These are all the derivatives of black coal-tar. But the future holds even more in store for us: for the formation of ring compounds by catalytic cyclization of petroleum hydrocarbons unfolds an inexhaustible, inexpensive source of aromatics (625).

## QUESTION REVIEW

### I. THE BENZENE RING.

**a. The benzene ring (640).**

1. Support the Kekule formula for benzene.
2. Show by means of structural formulas that ortho-di-chloro-benzene can be chlorinated to form *two* tri-chloro-benzenes. That the meta compound can form *three* tri-chloro-benzenes. That the para compound can form only *one* tri-chloro-benzene.

**b. Other ring compounds (641).**

3. Give the structural formulas for two substituted benzenes. For moth balls. For a ring compound which does not belong to the benzene series.

### II. PRODUCTS FROM COAL (642)

4. By a scale-drawing of a series of rectangles, show the relative quantities of products obtained from the destructive distillation of a ton of coal.
5. List the five fractions obtained from coal tar, giving three formulas for compounds obtained from three of them.

### III. PRODUCTS FROM COAL TAR.

6. Give one formula for each of the following: a dye, a drug, the ingredients of some plastic, an explosive.

**a. Dyes (643).**

7. Mention one interesting fact connected in this field with the following: alizarin, Perkin, von Baeyer, mordant, mercury, indigo, conscription in Syria, substantive dyestuff, indigo.

**b. Drugs (644).**

8. Describe the work which laid the basis for chemotherapy.

**c. Explosives (645).**

9. Write the formula for 2–4–6-trinitro-phenol. What is its common name? Write the formula for TNT, and give its chemical name.

**d. Plastics (646).**

10. Write the formula for styrene. For the ingredients of Bakelite.

**Reading References:** Articles in the Appendix:

*General:* 5, 60, 101, 245, 252, 318, 346, 406, 407, 408, 409, 411 and 416.

*Drugs:* 76, 150, 402, 405, 420 and 422.

*Dyes:* 3, 73, 101, 125, 148 and 150.

*Strategic materials:* 133, 140, 142, 145, 151, 252, 326, 340, 345, 411, 412 and 416.

## CHAPTER XLIV

## PLANT FOODS AND PLANT PRODUCTS

Plants and animals are coordinated in a never-ending cycle of life. Carbon dioxide, water and inorganic salts of nitrogen are converted, with the help of sunlight, into complex organic compounds, namely, carbohydrates, fats and proteins. At the same time, solar energy is stored up in the plant, *i.e.*, chemical bonds are formed in the plant products.

Animals, in turn, eat and assimilate these complex organic compounds. The solar energy is released, by breaking some chemical bonds to form new compounds, within the animal body. And the waste products of the animal eventually form the self-same, simple compounds with which the cycle began.

### THE FOOD OF PLANTS

**647. Photosynthesis.**—One of the most amazing chemical reactions in our living world is the transformation, in plants, of carbon dioxide and water into sugars, starches and cellulose. The process is called **photosynthesis** because it is effected by the aid of light.

**Chlorophyll,** the green coloring matter in plants, absorbs yellow and red light from the sun, and utilizes this solar energy to accomplish the syntheses of carbohydrates:

$$\underset{\text{solar energy}}{673{,}000 \text{ cals.}} + 6CO_2 + 6H_2O \rightarrow \underset{\text{sugar}}{C_6H_{12}O_6} + 6O_2.$$

No chemist has yet been able to duplicate this most important process, although Baly claims to have obtained certain sugar-like products by photochemical reactions. Perhaps some day this may be accomplished, and the acres of sugar cane and sugar beet will fall victim to the test-tubes of the scientist.

The carbon dioxide-oxygen cycle, of which photosynthesis is a part, has already been described (271).

**648. Inorganic Plant Foods.**—In addition to water and carbon dioxide from the air, the plant utilizes somewhat over a dozen of the 92 chemical elements, receiving them as inorganic salts from the soil.

Nitrogen, potassium and phosphorus are the three *indispensable* plant foods. In addition, rather *large quantities* of calcium, sulfur and magnesium are required. Finally, *traces* of a dozen other elements are found necessary for healthy plant growth; their exact functions are not precisely known. These latter include iron, manganese, copper, zinc, boron, iodine, etc., and vary somewhat for different plants.

A hundred years ago Liebig demonstrated the necessity of giving back to the soil by artificial means (*e.g.*, by fertilizers) the salts of phosphorus, nitrogen and potassium which are removed by the growth of plants.

**Nitrogen.** The nitrogen cycle (272) emphasizes the importance of this element in synthesizing **proteins** and promoting the growth of foliage in the living plant. It is estimated, for example, that a ton of wheat takes 47 pounds of nitrogen from the soil. Plant leaves cannot assimilate this nitrogen as they do carbon dioxide; for this reason fertilizers containing nitrates of sodium, calcium or ammonium, or calcium cyanamide, are added to the soil. The action of leguminous plants and the principle of **rotation of crops** has already been discussed (272). Alfalfa or sweet clover may "fix" as much as 300 pounds of nitrogen per acre.

**Potassium.** Though starches and sugars do not contain potassium, it is essential in some way to their production. Potash starvation reduces the vigor of the plant and makes it susceptible to attack by parasites. The chief potassium fertilizers are KCl (potash) and $K_2SO_4$; these have been mentioned elsewhere (307).

**Phosphorus.** This element stimulates the development of roots, makes for sturdy stalks, and hastens the process of ripening. It is supplied to the soil as fertilizer in the form of superphosphate of lime, or as other soluble phosphates; this, also, has been previously discussed (548).

A ton of barnyard manure contains about eight pounds of fixed nitrogen, six pounds of potash and six pounds of phosphates.

**649. Hydroponics.**—The chemical needs of the growing plant are revealed by the nutrient solutions used in soil-less gardening, or **hydroponics** (Greek, meaning *water-culture*). This science has been studied for several decades, but was popularized in 1937 by the investigations of E. Gericke in California, who succeeded in applying the methods to truck-farming. Tomatoes, for instance, bore enormous fruits nine months each year.

In this "dirtless farming," the plants are supported in sand or on a wire or cloth frame, so that the roots are immersed in a nutrient solution. Air must be blown through at frequent intervals.

A typical formula is given by J. W. Shive and W. R. Robbins, of the New Jersey Agricultural Experiment Station. Solution I contains 5.9 g. $KH_2PO_4$, 20.1 g. $Ca(NO_3)_2$, 10.7 g. $MgSO_4, 7H_2O$, and 1.8 g. $(NH_4)_2SO_4$ in 5 gallons of water. Solution II contains 0.8 g. each of $H_3BO_3$, $MnSO_4$, and $ZnSO_4$ in 1 pint of water. Solution III contains 0.8 g. $FeSO_4, 7H_2O$ in 1 pint of water. 10 cc. of solution II and 100 cc. of solution III are added to the 5 gallons of solution I immediately before use.

### PLANT PRODUCTS: CARBOHYDRATES

**650. Classes of Carbohydrates.**—The term "carbohydrate," as commonly used, refers to certain compounds containing carbon, hydrogen, and oxygen, which are among the chief products of vegetable life, and in which the ratio of hydrogen to oxygen is usually the same as in water $C_n(H_2O)_m$. These compounds might be represented, then, as being composed of carbon and water; hence the name "carbohydrate" (or hydrate of carbon): *e.g.*, the formula of glucose, $C_6H_{12}O_6$, might be written $6C,6H_2O$. This does not mean that a carbohydrate contains water, but only the elements of water.

The carbohydrates are divided into three classes:

**Sugars**
**Starch**
**Cellulose**

**651. Sugars.**—Sugars which contain carbon atoms in a single straight chain are called **monosaccharides.** The chain is from three to nine carbon atoms long. Of these, the hexoses $C_6H_{12}O_6$ are the most common; *e.g.*, glucose or grape sugar, fructose or fruit sugar (Fig. 212). A second class of sugars is the **disaccharides,** in which two monosaccharides are linked as illustrated in Fig. 212. Examples of these, with the formula $C_{12}H_{22}O_{11}$, are sucrose or cane sugar; maltose, formed by the action of malt or diastase on starch; and lactose or milk sugar, 5 per cent of which is present in cow's milk.

**Glucose, $C_6H_{12}O_6$.**—Glucose (*dextrose*, or *grape sugar*) occurs in many fruits, particularly the grape; hence its name. It is often associated with fructose in many sweet fruits and in honey. Glucose is manufactured on a large scale by boiling starch with a dilute acid, which plays the rôle of a catalyst:

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_x} + xH_2O \rightarrow \underset{\text{Glucose}}{xC_6H_{12}O_6}.$$

After neutralizing the acid, glucose may be obtained as a crystalline mass by evaporating the solution. Corn syrup contains glucose, dextrin, and water.

Pure glucose is colorless, and is quite soluble in water. Although it is not so sweet as cane sugar, glucose is used extensively in jams, jellies and in the manufacture of confectionery.

**Sucrose, $C_{12}H_{22}O_{11}$.** Ordinary sugar, or sucrose, is found chiefly in the sugar cane and the sugar beet; it also occurs in the sugar maple and in honey.

The sugar cane was originally grown in India and Arabia and was introduced into Southern Europe by the Arabs. The sugar cane contains from 16 to 18 per cent of sugar. Sugar was discovered in beet root by the German chemist Marggraf in 1747. At that time there was about 6 per cent of sugar in the beet, but by cultivation the percentage has been increased to 13 to 16.

Sugar is obtained from the sugar cane by crushing the stalks between rollers; but the beet roots are cut into slices, and the sugar extracted by a diffusion process. After appropriate preliminary treatment, the sugar solution is evaporated under reduced pressure at about 65° to prevent decomposition of sugar. The syrup obtained, upon cooling, yields crystals of brown sugar, which can be refined by dissolving in water, filtering through boneblack, and evaporating in vacuum pans until sugar crystallizes out. Production statistics are given in Table 124.

TABLE 124. WORLD PRODUCTION OF SUCROSE

| *Year* | *Cane Sugar* | *Beet Sugar* |
|---|---|---|
| 1922–3 | 15,130,000 tons | 5,850,000 tons |
| 1932–3 | 18,759,000 " | 8,786,000 " |
| 1938–9 | 22,689,000 " | 11,500,000 " |

1939–40 in thousands of short tons: U. S. A. 1,719 beet, 511 cane; Cuban cane 3,124; European beet 10,864; British India cane 5,093.

Sucrose is very soluble in water, and it melts at 160°. When sugar is heated from 200° to 210°, it loses water, being gradually converted into a brown mass known as *caramel.* This substance is used for coloring liquors and soups.

**Invert sugar.** When sucrose is boiled with water containing a little acid, the hydrogen ion of the acid acts as a catalyst, and the sugar is hydrolyzed to glucose and fructose ("invert sugar"):

$$C_{12}H_{22}O_{11} + H_2O \rightarrow \underbrace{\underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}}_{\text{Invert Sugar}}.$$

The mixture of the isomers glucose and fructose is a sticky mass, which is used in the manufacture of preserves, confectionery, etc. Crystallization of either of the two sugars, in the mixture, is slow because the large molecules of each sugar interfere with the crystallization of the other sugar. Invert sugar is therefore used in making soft candy, or candy that is to be "pulled."

**652. Reducing Sugars.**—Some sugars act chemically as reducing agents.

DEMONSTRATION 163. REDUCING SUGARS

Materials: Solution A containing 69.3 g. $CuSO_4$, $5H_2O$ plus 1,000 cc. of water. Solution B contains 350 g. Rochelle salt plus 100 g. NaOH plus 1,000 cc. of water. 10 per cent glucose solution. 1 N $AgNO_3$.

Glucose, unlike cane sugar, reduces cupric sulfate to a yellow precipitate of cuprous oxide, $Cu_2O$, which rapidly turns red. When a mixture of equal quantities of solutions A and B (**Fehling's solution**) is heated with a few cc. of glucose solution, this change is brought about, and a red precipitate of $Cu_2O$ is formed. This reaction is utilized in the analysis of urine for the detection of **diabetes mellitus.** In this disease an abnormal quantity of glucose appears in the urine, sometimes as much as 10 per cent. This is due to an insufficient supply of **insulin** from the pancreas, in the absence of which the carbohydrates are not thoroughly burned. When this metabolism of sugar fails, utilization of fats and proteins also fails. Today, thanks to the brilliant researches of Best, Banting and others in isolating insulin, a person suffering from diabetes can be transformed into a normal, healthy individual by the daily use of insulin.

The reducing action of these sugars is also illustrated when 100 cc. of glucose solution is added to an equal volume of silver nitrate solution. Within a few minutes the silver ion, $Ag^+$, is reduced to metallic silver, $Ag^\circ$, and a shiny mirror is coated out on the inner surface of the container.

**653. Structure of Sugars.**—Intensive research on the structures of sugars has established many of their formulas. A few examples are given in Fig. 212.

By placing the H or OH groups on different sides of the molecule, 32 different sugars with formulas corresponding to that given for glucose may be obtained. They are **isomers** of one another.

Also, the position of $-O-$, forming what is called a **lactone ring**, determines other properties of the sugar. Depending upon the location of this ring, a water solution of the monosaccharide will rotate polarized light to the right (dextro-rotary or *d*-glucose), or to the left. Such isomers are called **optical isomers**; and this property of rotating the plane of polarization is of considerable value in identifying and studying the sugars.

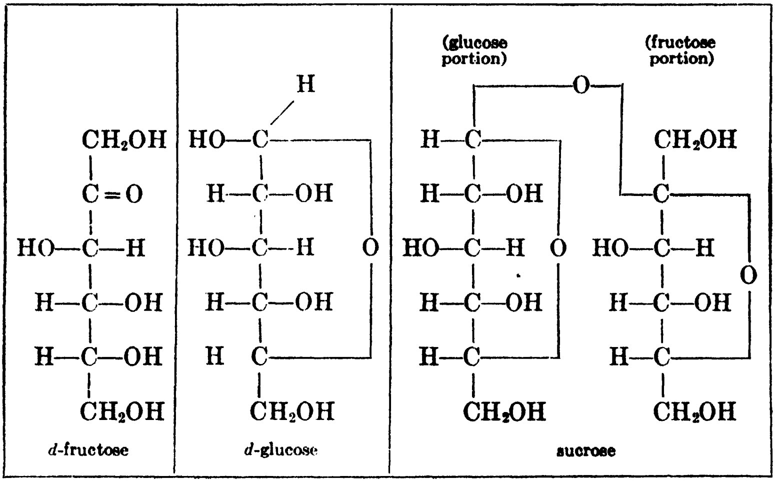


FIG. 212. Some Common Sugars.

The structure of sucrose, as indicated in Fig. 212, is in accord with the fact that the inversion of this sugar forms a mixture of glucose and fructose; it simply indicates that rupture occurs at the —O— link.

**654. Starch, $(C_6H_{10}O_5)_x$.**—Starch is the most abundant of all foods, as is indicated by the composition of the following foodstuffs:

| | |
|---|---|
| Potato | about 20% starch |
| Wheat | 65% " |
| Maize (corn) | 65% " |
| Rice | 80% " |

Like sugar, it is formed from carbon dioxide and water by the process of photosynthesis. It, and cellulose, are called *polysaccharides.*

Starch consists of minute colorless granules, which differ somewhat in appearance according to the source. Thus, the granules may be round, elliptical, or angular, and they consist of concentric layers or rings arranged round a nucleus.

In the United States starch is obtained chiefly from maize, whereas potatoes are the chief source in Germany, and rice in England. The process of manufacture is largely mechanical. The softened or crushed material is washed, permitting the granules of starch to pass through a fine wire or silk sieve, and leaving the gluten behind.

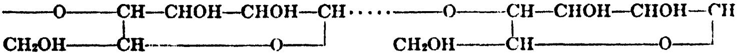
Starch is insoluble in cold water, but when it is treated with hot water the granules burst and the substance goes into colloidal solution, *i.e.*, the very finely divided particles are suspended in water. Colloidal solutions of starch are used in the laundry. Colloidal starch turns blue in the presence of iodine (delicate test). When, therefore, iodine is dissolved in a solution of potassium iodide and some of the brown solution placed on a plant, *e.g.*, the leaf, the granules of starch turn blue, while the other parts are not affected.

Starchy foods are made more digestible by cooking. During the process of digestion, starch is first converted into the simpler sugars by the agency of the digestive fluids.

Starch is the starting point in the manufacture of large quantities of alcohol and alcoholic beverages.

**Dextrin** $(C_6H_{10}O_5)_n$ may be obtained by gently heating starch (210°), or by moistening starch with a mixture of dilute nitric and hydrochloric acids, and heating from 100° to 125°. It is sold under the name of **British gum**, and when treated with water it forms a clear mucilage.

**655. Cellulose,** $(C_6H_{10}O_5)_y$.—As its name implies, cellulose forms cell walls, constituting the framework of most vegetable tissues. It is an aggregate of disaccharide-like units (cellobiose) arranged in long chains, often cross-linked. X-ray examination indicates that about 50 of these units are joined to form a bundle or micelle; and cellulose fiber is made up of a large number of these micelles. (Fig. 213.)

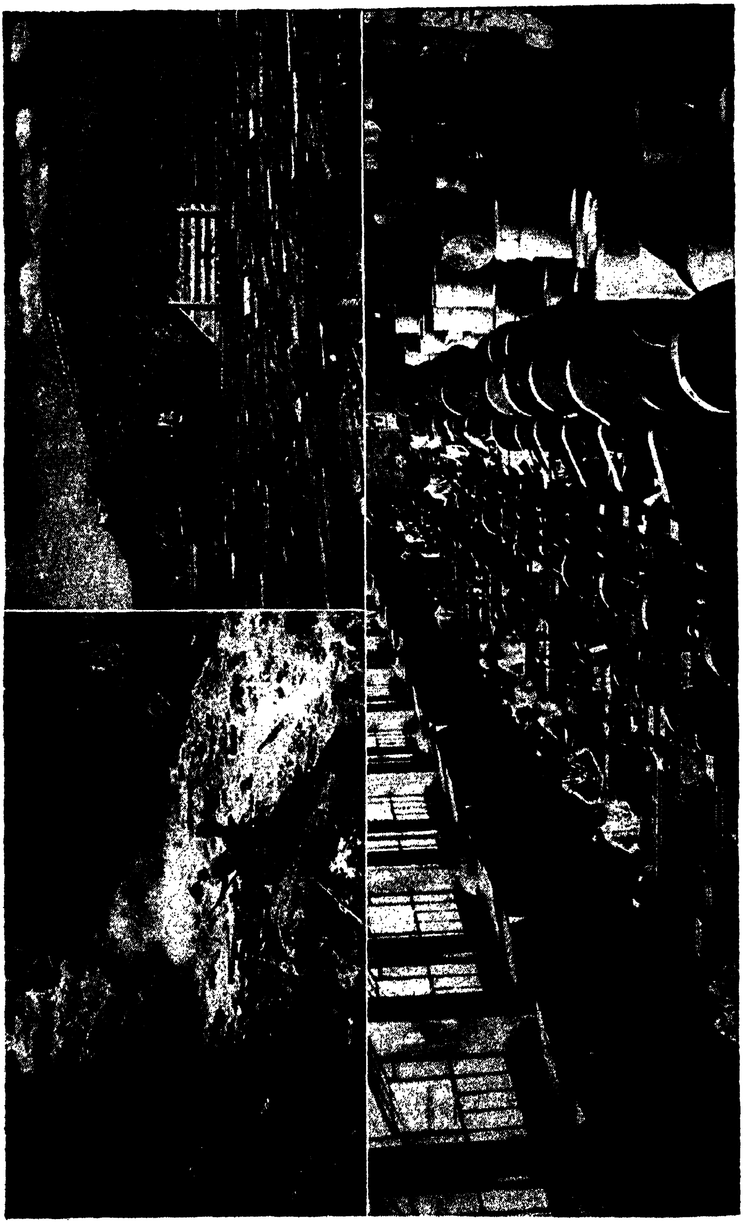


$$\begin{array}{l} \text{——O——CH—CHOH—CHOH—CH}\cdots\text{——O——CH—CHOH—CHOH—CH} \\ \text{CH}_2\text{OH——CH————O——} \qquad \text{CH}_2\text{OH——CH————O——} \end{array}$$

FIG. 213. A cellobiose unit.

**Wood.** This is the raw material from which paper, sugar, and some rayon is manufactured. Wood consists of cellulose fibers intermixed with lignin.

Since the cellulose unit contains a saccharide, it is not surprising that sugar may be made from sawdust. According to this process (Bergius) the sawdust is heated under pressure in the presence



*Courtesy of the Brown Company*

FIG. 214. Steps in the manufacture of paper.

of an acid and steam; a monosaccharide is formed. Also, by the fermentation of this sugar, ethyl alcohol is produced:

$$\underset{\text{cellulose}}{C_6H_{10}O_5} \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6} \rightarrow \underset{\text{ethyl alcohol}}{C_2H_5OH}.$$

It is estimated that the waste paper-pulp liquor in Sweden would supply sufficient power alcohol by this process to replace 200,000,000 gallons of gasoline annually.

**Paper.**—As previously stated, paper is produced principally from wood fiber. The production of paper is partly a chemical process, being more complicated when wood, straw, and grass are used as a source of the fiber than when rags are used.

The raw materials are first "cooked" with appropriate chemicals in order to secure the fiber. With wood the sulfite process is most widely employed. The chemical dissolves the non-cellulose components, such as lignin, leaving the more resistant cellulose. The fiber is thoroughly washed with water and the material screened. The fiber is then bleached by means of a hypochlorite or chlorine. It is next beaten in tubs, dyed if a colored product is wanted, and then sized. **Sizing** prevents the spreading of ink, which is an essential quality of writing paper, but not for newspaper. Sizing is accomplished by means of such substances as rosin and alum, which are passed into the beater with the pulp. Paper may be **"loaded"** by adding pulverized gypsum and certain other white substances; and it may be given a smooth surface by treatment with casein, a product from milk.

Paper is manufactured by means of machines, which are from 100 to 240 inches wide. These produce paper continuously. A large paper machine has a capacity of about 150 tons in 24 hours, and can produce paper at the rate of more than 1,000 feet per minute.

**Cotton.** Cotton is almost pure cellulose. When cotton cloth is treated with a solution of sodium hydroxide, it takes on a high silky luster, the process being known as **mercerization** (John Mercer, 1844). The cloth is stronger, more durable, and has an increased affinity for many dyes. Cotton cloth is not soluble in a boiling solution of sodium hydroxide; in this respect it differs from animal fibers (and from cellulose trinitrate) which will dissolve completely. This test may be applied to estimate the quantity of cotton in a purported "all-wool" fabric.

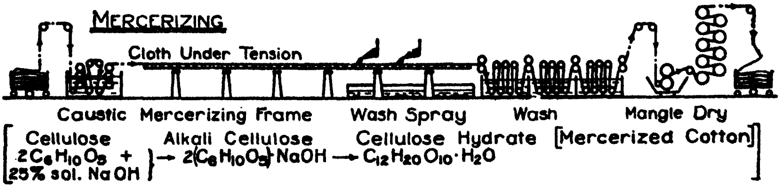


FIG. 215. Mercerization of cotton cloth.

**Rayon.** The production of this synthetic fiber has made astonishingly rapid progress in the past decade. Of several processes, the **viscose process**, discovered by Cross and Bevin in 1892, is the most important. In this method, sulfite pulp from spruce, or purified cotton linters, or a mixture of these, is treated with a solution of sodium hydroxide; this is pressed into sheets of pulp. The pulp is shredded into "crumbs" which are treated with carbon disulfide, and aged. This produces an orange-colored product, cellulose xanthate. The xanthate is dissolved in a dilute solution of sodium hydroxide, forming a sirupy liquid, "viscose." The latter is ejected through minute orifices (*e.g.*, perforations in platinum-gold alloys, or, recently, plastics) into an acidic bath, such as a solution of $NaHSO_4$, where the cellulose is produced as filaments (Fig. 217).

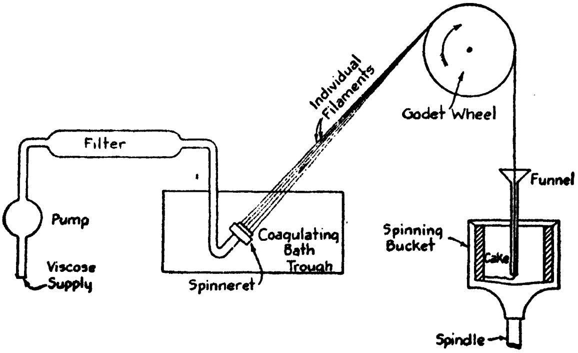
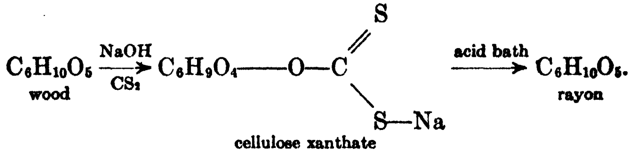


FIG. 216. Formation of viscose rayon.



$$\underset{\text{wood}}{C_6H_{10}O_5} \xrightarrow[CS_2]{NaOH} \underset{\text{cellulose xanthate}}{C_6H_9O_4{-}O{-}C\begin{matrix}\diagup\!\!\!\!\diagup S \\ \diagdown S{-}Na\end{matrix}} \xrightarrow{\text{acid bath}} \underset{\text{rayon}}{C_6H_{10}O_5.}$$

FIG. 217. Viscose process for manufacturing rayon.

These filaments are collected on bobbins, washed, desulfurized and bleached. Rayon may be dyed most beautifully.

The intense activity for national self-sufficiency has led, during the past decade, to extraordinary developments in the raw materials now being used for cellulose fibers. The Pomilio cellulose

(Viscose) process, for instance, has expanded from Italy throughout the civilized world, making rayon from corn, rice, oats, straw, esparto, Italian cane, Cunso fir-tree cellulose, sugar-cane bagasse, and so forth. In September 1938 the Snia Viscosa opened a factory for making rayon from marsh grasses near Venice: the main building is nearly a mile long.

**Cellophane.** The word "cellophane" means "cellulose glass." It is essentially a transparent film of regenerated cellulose, usually produced by the viscose process. A thin sheet of viscose solution is ejected through a suitable nozzle into a coagulating bath. In manufacturing cellophane sausage casings, the viscose solution is forced through a die, a continuous tube being obtained.

**Cellulose esters.** Approximately one-fifth of the rayon produced is **cellulose acetate** rather than regenerated cellulose.

The acetate ester is produced by treating purified cellulose, usually cotton linters, with a mixture of acetic anhydride and glacial acetic acid in the presence of sulfuric acid or zinc chloride. A thick paste is obtained. The paste is dissolved in acetone and ejected through fine orifices into warm air: the acetone evaporates, and is recovered.

Cellulose acetate fibers differ markedly from regenerated cellulose rayons in their behavior towards dyes. Cellulose acetate is used also in safety motion-picture film, because cellulose acetate, unlike cellulose nitrate, is relatively non-inflammable.

**Nitrocellulose** is another important ester which has already been discussed in some detail (**535**). It is used extensively in the manufacture of collodion, celluloid, explosives, lacquers, and so forth.

## QUESTION REVIEW

### I. THE FOOD OF PLANTS.

**a. Photosynthesis (647).**

1. Write an equation representing the photosynthetic process.
2. If the solar energy consumed in forming 1 kilogram (2.2 pounds) of glucose were used to heat water, what weight of ice-water could be brought to boiling?

**b. Inorganic plant foods (648).**

3. Name three elements which are indispensible plant foods. Two more required in large quantities. Three required in traces. In each case state the form in which the element is made available to the plant.
4. A farmer buys a ton of phosphates and an equal quantity of potash. If he had bought manure instead, how much would he have needed?

**c. Hydroponics (649).**

### II. PLANT PRODUCTS: CARBOHYDRATES.

**Classes of carbohydrates (650).**

**a. Sugars (651–653).**

5. Give the formula for a "pentose." Draw possible structural formulas for two pentoses.
6. Contrast in detail the properties of glucose with those of sucrose.
7. Has cane or beet sugar made the greater progress during the past two decades?
8. Describe an experiment which shows the reducing properties of glucose. To what important use is this property put?
9. Identify: lactone ring, invert sugar, caramel, dextrose, disaccharide, isomer, optical isomer, monosaccharide, Fehling's solution.

**b. Starch (654).**

10. How is starch manufactured? How may it be detected in the plant?

**c. Cellulose (655).**

11. What is: cellobiose, paper, cellophane, wood, acetic anhydride, viscose, micelle, mercerization, cellulose xanthate, sizing, lignin?

12. Give equations showing how paper may be transformed into alcohol.
13. Outline the viscose process for making rayon.
14. Outline the steps for making cellulose acetate.

**Reading References:** Articles in the Appendix:

*General:* 2, 6, 18, 38, 42, 220, 226, 256 and 415.

*Paper:* 24, 246, 327 and 338.

*Strategic materials:* 133, 140, 142, 145, 151, 252, 326, 340, 345, 411, 416 and 420.

*Textiles:* (*cellulose*): 14, 25, 110, 120, 125, 224, 250, 255, 311 and 333; (*protein*): 25, 80, 146, 220, 226, 250, 255, 324 and 409.

# CHAPTER XLV

# ANIMAL FOODS AND ANIMAL PRODUCTS

## The Food of Animals

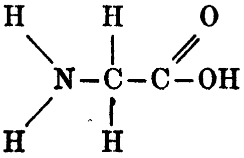
**656. Introductory.**—Animals are dependent upon plants for their food; also, the food of animals is, as a rule, much more complex than that of plants. The proteins, carbohydrates, and fats are characterized by their high molecular weights, and some of them have very complicated structures.

**657. Proteins.**—The word *protein* is derived from a Greek word meaning "to take the first place," because the great physiological importance of this group of substances was early recognized. Proteins are found in all living matter, and are found therefore in varying amounts in all natural foodstuffs. Since they form the main constituents of living animal tissues, they are most plentiful in animal foods such as meat, eggs, fish, etc. *All proteins contain carbon, hydrogen, nitrogen, oxygen, and sulfur, and a few contain phosphorus.*

A great deal has been learned during the past decade concerning the sizes of the giant protein molecules. Most of these molecules are colloidal (664); such particles suspended in water settle out very slowly indeed. The. Svedberg, in 1926, received a Nobel Prize for his "ultra-centrifuge," an apparatus which whirls protein suspensions at tremendous velocities, photographing them during the process. Over a period of several hours the protein molecules settle; the rate of settling indicates their molecular weights. Some values obtained by this method are: egg albumin, 34,000; hemoglobin 68,000, casein 192,000.

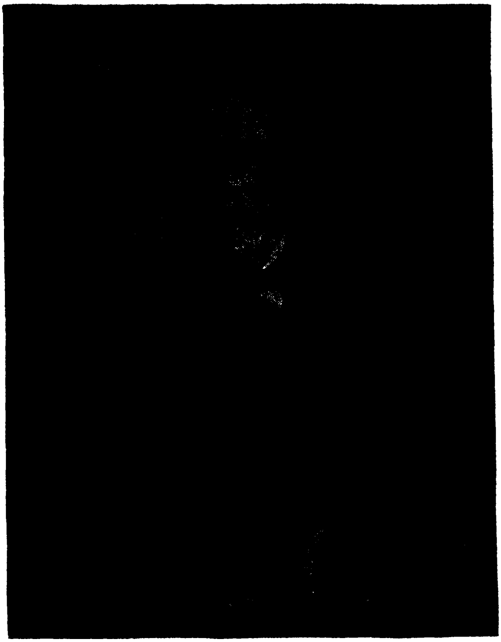
Recent work with the electron microscope on large proteins, such as the tobacco mosaic virus protein, is reported elsewhere (94).

During digestion, giant protein molecules are hydrolyzed into simpler substances, such as the **amino-acids.** These acids contain the amino group, $-NH_2$ and the acid or carboxyl group, $-COOH$. A very simple amino-acid is



or $NH_2-CH_2-COOH$

glycine



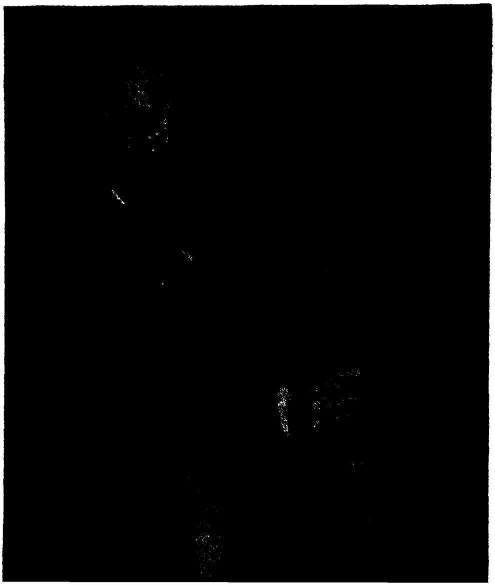
(1822–1895)

Pasteur was first stimulated to a scientific career by the chemistry lectures at the Sorbonne by J. B. Dumas. In 1848 Pasteur published his first major research: the separation of the optical isomers of tartaric acids. That year he became professor of physics at Dijon, and a year later professor of chemistry at Strasbourg. As professor and dean at Lille (1854), he showed that the fermentation of beer, wine and milk was due to a micro-organism. From this research, his interest extended along those biological lines for which he is best known: silk-worm disease, sheep anthrax, and rabies. Struck with semi-paralysis in 1868, Pasteur kept bravely on. At the dedication of the Pasteur Institute in 1888 he wrote: "Science, in obeying the law of humanity, will always labour to enlarge the frontiers of life."

### EMIL FISCHER

(1852–1919)

Noted organic chemist, whose skill and brilliant researches attracted a constant stream of able pupils to the University of Berlin. For eight years he was assistant to von Baeyer at Munich. Fischer established the structures of many extremely complex organic molecules, including sugars, ferments, dyestuffs, and proteins, in particular osazones, purines, and the synthesis of polypeptides simulating natural proteins. He received the first Nobel Prize in Chemistry (1902), and numerous other awards from scientific societies all over the world.



While it is known that proteins are built up of these simple amino-acid units, such as glycine, no chemist has yet been able to synthesize the huge protein molecules now produced every day by the human body. Emil Fischer (see portrait) has contributed more than any other scientist to an understanding of these complicated proteins.

Iron, copper, manganese, zinc, and iodine are found in small quantities in certain proteins. Iodine, for instance, is found in the thyroid gland.

The body obtains proteins from albuminous or nitrogenous foods, such as lean meat, egg white, fish, the gluten of flour, etc. Milk is especially valuable, particularly for the young. These proteins build and repair tissues; and if only a little fat and carbohydrate is present, proteins may also serve as fuel. The American beef-eater obtains his proteins from meat; the Oriental obtains the same body-food from soy flour, which is high in protein content.

**658. Carbohydrates and Fats.**—Carbohydrates (650) and fats (637) are the chief sources of body energy. Fats yield about 4000 calories per pound, and proteins and carbohydrates about 1800 calories per pound. This is true whether the compound is burned in the body, or in a bomb calorimeter.

The athlete has a quick supply of energy about half an hour after eating sugar; but for sustained effort, the diet should contain at least 25 per cent of its energy in the form of fat. From this statement, it is apparent that fat is more sustaining; which indicates that a hibernating animal is supplied with energy for a long period of time by the slow oxidation of stored-up fat.

Oils are more easily assimilated than solid fats; also, the presence of carbohydrate or proteins assists in the complete oxidation of the fat.

The food requirements of each individual are obviously dependent upon a great number of factors, *e.g.*, weight, age, occupation, etc. The diet of an "average man" at moderate work should be that given in Table 125, which was compiled by the Food Committee of the Royal Society.

TABLE 125. DAILY FOOD REQUIREMENTS FOR AN AVERAGE MAN

| | | | | |
|---|---|---|---|---|
| Proteins | 70 g. | 280 cals. | Calcium | 0.68 g. |
| Fats | 90 g. | 810 cals. | Phosphorus | 1.32 g. |
| Carbohydrates | 550 g. | 2,200 cals. | Iron | 0.015 g. |

Under ordinary conditions 10 per cent should be added to the above figures to allow for food which escapes assimilation.

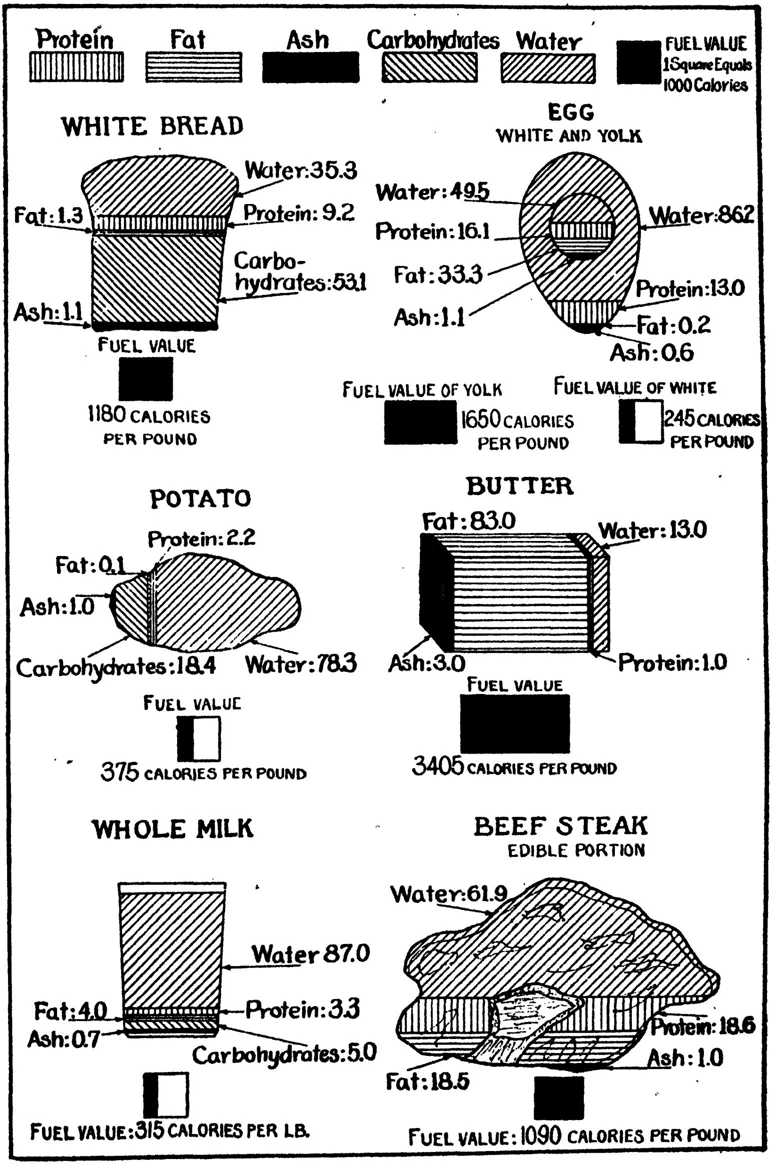


FIG. 218. Fuel value and compositions of some common foods.

*Question*: calculate these values in terms of pounds (1 pound equals 453.4 grams). Refer to Fig. 218 and estimate how much beef-steak, butter, and potato supply the necessary number of proteins, fats and carbohydrates respectively.

**659. Mineral Matter.**—To keep the body in health, it is necessary that it be supplied with an adequate amount of mineral matter. In the case of rickets there is a marked disturbance in the assimilation of calcium and phosphorus. These elements are especially necessary for the growing child in order that the skeleton may be properly formed. Calcium is the element which is most constant in amount in the blood. In case of rickets, the phosphorus content of the blood is below normal. Calcium and phosphorus are supplied by milk. Cheese is rich in calcium. Phosphorus is supplied by many other foods, such as eggs and meats; but in many cases the diet is deficient in calcium, as in the white bread, meat, potato, and sugar diet. Of the vegetable foods, only the leaves of plants are rich in calcium; they are also rich in vitamins. The leaves of certain plants are, indeed, a complete food.

**660. Vitamins.**—Since the pioneer work of Hopkins, of McCollum, and of Funk (1912) it has been realized that animals require certain *accessory food factors* called **vitamins.** These substances are present in traces in nearly all fresh foods. They are recognized less by their presence than by the deleterious effects which their absence induces. Nevertheless they are definite chemical compounds; many of them have been synthesized in the laboratory (Fig. 219).

It is well-nigh impossible for the beginning student to grasp the enormous problems which the identification and synthesis of a vitamin entails. First, in detecting its existence through its physiological reactions white rats, chickens and other animals must be fed a carefully controlled diet lacking in the supposed vitamin. Reaction of the animal to this strange diet is painstakingly diagnosed. Then the diet is changed, so as to include the vitamin in question, and the restoration of health is noted. Following this, the vitamin itself must be concentrated, each stage in the concentration being controlled by more time-consuming dietary tests. This concentrate is small indeed, for the vitamins are so potent. For example, in the synthesis of pantothenic acid (*vide infra*) 5 mg. of concentrate, scarcely more than a pin-head of substance, was obtained from 2 tons of rice bran. Yet, by working with this minute quantity of material, the organic chemist was able to determine its chemical structure, and to reconstruct a similar molecule in the laboratory.

In a field which is rapidly changing, it will suffice to summarize a few salient facts about each of these vitamins. Also, the chemical structures of these important compounds is given, for reference only, in Fig. 219. By 1941 eight vitamins had been synthesized, and thiamin chloride, riboflavin, nicotinic acid, pantothenic acid, alpha-tocopherol and vitamin $K_1$ had been placed in commercial production.

**Vitamin A.** This important vitamin promotes growth and increases resistance to sinus infections. The glare of automobile headlights along a modern highway temporarily destroys the visual purple in the eye; presence of Vitamin A quickly restores the equilibrium, while lack of this vitamin produces "night blindness." Other eye diseases follow.

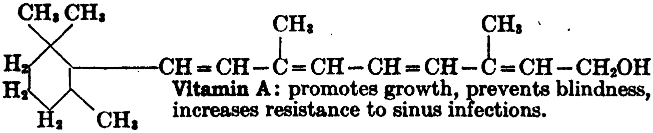
The vitamin is manufactured in the animal from the orange coloring matter, carotene, which occurs in carrots and leafy green vegetables:

$$\underset{\text{carotene}}{C_{40}H_{56}} \xrightarrow{+2H_2O} \underset{\text{vitamin A}}{2C_{20}H_{29}OH}$$

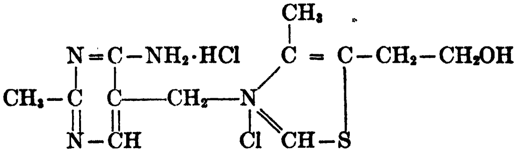
Cows and fish carry out this same synthesis of Vitamin A, and store it in milk or in fish-livers, a rich source of the vitamin for man. Children, in particular, require these foods.

**Vitamin B.** This proved to be a mixture of several vitamins, and is now spoken of as the **vitamin B complex.** **Vitamin $B_1$** or **thiamin chloride** prevents neuritis and loss of appetite. R. R. Williams, investigating the occurrence of a nervous disease, beriberi, in the Philippines amongst natives who had been fed polished rice, demonstrated the presence of $B_1$ in the discarded rice husks, and finally established the structure of this important compound. Whole wheat bread and vegetables provide $B_1$ although it is lacking in refined mill flours. **Vitamin $B_2$** (vitamin G) or **riboflavin** is essential for growth and for a healthy condition of the skin.

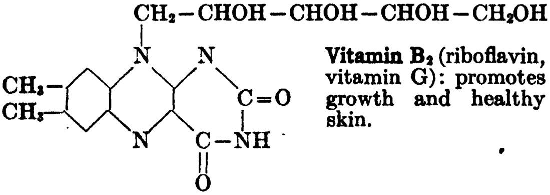
**Nicotinic acid,** related to nicotine, prevents pellagra; this affliction is characterized by digestive disturbances, skin eruption, and nervous disorders leading to insanity. **Vitamin $B_6$,** isolated by three independent research groups in 1938, was established in 1940. It is reported to cure skin eruptions (dermatitis) and also to stimulate growth. **Pantothenic acid** (Greek, *everywhere*), studied by the brother of R. R. Williams, was synthesized by



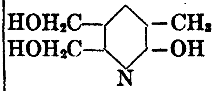
**Vitamin A:** promotes growth, prevents blindness, increases resistance to sinus infections.



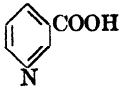
**Vitamin B₁** (thiamin): prevents neuritis, increases appetite.



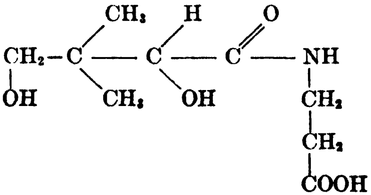
**Vitamin B₂** (riboflavin, vitamin G): promotes growth and healthy skin.



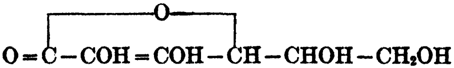
**Vitamin B₆:** promotes growth, cures dermatitis.



**Nicotinic acid:** prevents pellagra.

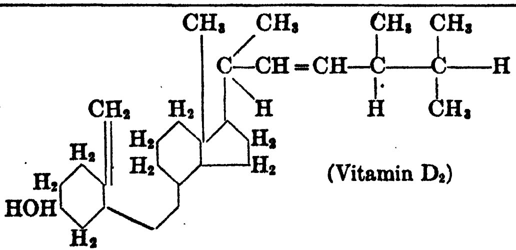


Pantothenic acid: chick anti-dermatitis factor.



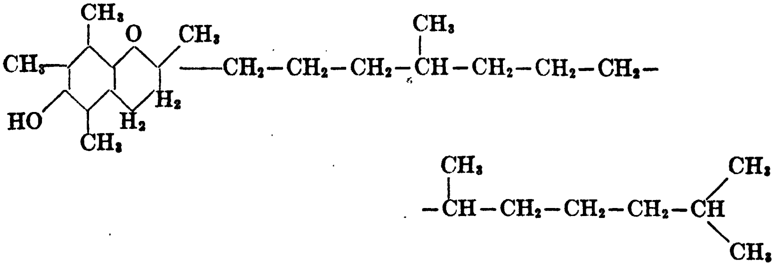
$$O=C-COH=COH-CH-CHOH-CH_2OH$$

**Vitamin C:** prevents scurvy. Also, with D promotes sound teeth and general good health.

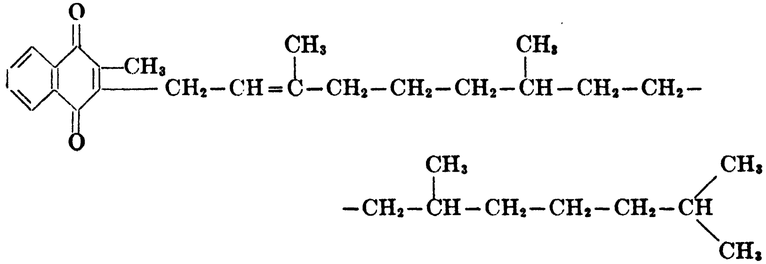


(Vitamin $D_2$)

**Vitamin D:** prevents rickets.



**Vitamin E** (α-tocopherol): prevents sterility, controls lactation.



**Vitamin $K_1$:** prevents bleeding.

FIG. 219. The chemical structures and functions of the vitamins.

Vitamins H, $L_1$, $L_2$, M, P (citrin) are also known.

Merck and Company in 1940. It is spoken of as the "chick antidermatitis factor." In the vitamin B complex there is also a **filtrate factor,** the chemistry of which still remains unsolved.

**Vitamin C.** This is the scurvy-preventing (*antiscorbutic*) vitamin.

Scurvy was known to the Greeks and other ancient people. It has been very common in armies and navies. Captain Cook, in 1772, recognized the value of fresh food and citrus fruits and therefore supplied his crew with them. During his voyage of three years there was an absence of scurvy. Recognition of the vitamin character of the substance which prevents scurvy was not accomplished, however, until 1919.

Vitamin C is the least stable of the vitamins, and is destroyed during the cooking or canning of foods, unless air is excluded. In this connection, the use of pasteurized milk by children should be counteracted by including fruit juices in their diets.

**Vitamin D.** This is the *antirachitic vitamin*, or the one which prevents rickets, a disease very common to children, particularly in certain industrial districts. Children suffering from rickets are unable to assimilate calcium and phosphates in building strong, sturdy bones. There are several vitamin Ds, *i.e.*, $D_1$, $D_2$, $D_3$, $D_4$, etc., a number of which have been identified by Windaus. They differ from one another as regards side chain structure. Vitamin D, in conjunction with vitamin C, builds better teeth and promotes general good health.

Rickets do not occur in the Arctic regions where the food is chiefly fish. In fact, vitamin D is present in such quantities in fish oils that the Canadian Government collects 200,000 gallons of cod-liver oil each year.

The disease is likewise uncommon in the tropics, where the body is subjected to intense solar radiation. This interesting observation was explained in 1927, when it was discovered that *ergosterol*, a substance present in fats in the skin, is converted into vitamin D (*viosterol*) upon irradiation with ultra-violet light. The irradiation of milk and other foods containing ergosterol achieves this same purpose, as well as the irradiation of the foods fed to cows.

**Vitamin E.** Vitamin E, alpha-tocopherol, the essence of fertility, was synthesized in 1938 by Smith at Minnesota in collaboration with Merck and Company, by Bergel and Todd in England and by Karrer in Zürich. It is found in wheat germs, lettuce, and in the oils extracted from certain grains. Though its absence results in sterility, Vitamin E apparently influences the general functional activity of the cell rather than the direct reproductive process. It also controls lactation in mother animals.

**Vitamin K.** This is the anti-bleeding vitamin. By 1939 Doisy and his co-workers at St. Louis University had isolated two factors (*i.e.*, $K_1$ and $K_2$) from alfalfa. New-born infants do not produce the vitamin $K_1$ during the first ten days of their lives, so that it has now become routine hospital practice to inject the vitamin into the baby shortly after birth, thereby decreasing the deaths which frequently result from internal bleeding during these first few days of the child's life. Although injection in the blood stream may hasten clotting during surgical operations, the K vitamins do not seem to hold much promise to save those who have inherited hemophilia.

## Animal Products

**661. Enzymes.**—Within the body there are a number of organic catalysts which control the processes of assimilation of our food. They are called **enzymes**; and each has its own particular function. Within the past decade the chemical structures of many of them have been elucidated, and a number (*e.g.*, pepsin, trypsin) have been prepared in a pure, crystalline form (Northrup).

As the food passes into the mouth, **ptyalin** and **maltase** in the saliva make starch soluble, and finally convert it into glucose. **Pepsin** in the gastric juice converts albuminous matter or proteins into soluble peptones or amino-acids, preparatory to their absorption through the cell walls. Further along, in the small intestine, pancreatic **trypsin** completes the conversion. **Lipase** in the gastric juice and **steapsin** in the pancreatic juice hydrolyze emulsified fat (*e.g.*, in milk) into fatty acids and glycerine; in this form these two products can diffuse through the intestinal wall, after which they recombine to form fat in the blood. **Amylopsin** of the pancreatic juice splits starch.

**662. Hormones.**—In addition to the vitamins, which are usually produced outside of the body and then acquired by the food we eat, there is a whole class of body regulators formed *within* the living animal. These substances, named **hormones** (Greek, *excite*). They control eight specific biological processes: growth, sex characteristics, metabolism, digestion, production of milk, nerve and heart action, and skin processes.

When an animal is suddenly frightened, the hormone **adrenalin** is secreted by the supra-renal glands. This augments the sympathetic nervous system, contracts the blood vessels (thereby increasing blood pressure), speeds up heart action, and releases glucose from the liver as an immediate source of extra energy. This constrictor property of adrenalin is useful to the surgeon in stopping the flow of blood. So potent is the hormone that the biological effects of one part in 300,000,000 parts of water may be detected. The structure of adrenalin was established in 1905; and today it is manufactured synthetically, as well as extracted from glands.

Two other hormones have been mentioned previously: **thyroxin** (612), a secretion of the thyroid gland which controls metabolism; and **insulin**, a secretion of the pancreas which controls the combustion of carbohydrates. Both of these hormones are proteins.

The properties of some other hormones, whose structures have not yet been fully established, are of considerable current interest. **Prolactin**, crystallized by White of Yale, regulates the flow of milk in mother animals; **heparin** is anti-blood-clotting and retards cell growth; another hormone isolated by Laofburow is used to stimulate growth of epithelial cells after severe burns, and **corticosterone** prevents post-operative shock and shell shock. Then there are so-called **anti-hormones**: one which prevents the formation of insulin, another known as the anti-gonadotropic factor.

In recent years considerable interest has focussed upon the hormones which control sex characteristics. The production of these hormones is especially enhanced during puberty and child-bearing, a fact which is utilized in detecting pregnancy. **Gonadotropic** hormones released by the pituitary glands pass along the blood stream to the sex glands, stimulating these latter organs to produce both male and female sex hormones.

Of the *male* hormones the most important are **androsterone** and **testosterone**. These control the development of male characteristics. The latter is the more active. Of the *female* hormones the two most important are **theelin (oesterone)** and **progesterone**. The development of the breasts is under the influence of theelin and progesterone. Theelin increases the growth of the mammary ducts, progesterone enlarges the ends of the ducts. The actual formation of the milk is controlled by another hormone, **prolactin.**

Theelin also prepares the uterus, during the fortnight before ovulation, to receive the egg; progesterone thickens the walls of the uterus and prevents miscarriage.

It is also possible that theelin and androsterone determine the sex of the embryonic organism.

The structures of these different hormones is surprisingly similar, as is illustrated in Fig. 220. They all belong to a class of compounds known as the **steroids.**

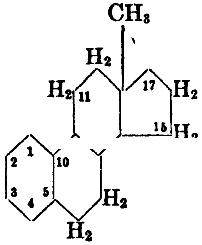
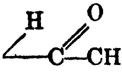


FIG. 220. Basic pattern for some sex hormones.

The radicals substituting in numbered positions are:

| | | 1 | 2 | 3 | 4 | 5 | 10 | 17 |
|---|---|---|---|---|---|---|---|---|
| male | androsterone | $H_2$ | $H_2$ | HOH | $H_2$ | H | $CH_3$ | O |
| | testosterone | $H_2$ | $H_2$ | O | H | — | $CH_3$ | HOH |
| female. . | progesterone | $H_2$ | $H_2$ | O | H | — | $CH_3$ |  |

Theelin differs from the preceding three in that its 1–5 ring is unsaturated (*i.e.*, it is aromatic, like benzene). The groups substituted in theelin are: (1) H; (2) H; (3) OH; 4 (H); (17) O. Write the structural formulas for androsterone and for theelin, showing their differences (include all bonds).

**663. Protein Fibers.**—Cellulose fibers from the vegetable kingdom (*e.g.*, cotton, rayon, cellulose esters), and protein fibers from the animal kingdom (*e.g.*, silk, wool) have lately been supplemented by hydrocarbon fibers (*e.g.*, plastic fibers such as Vinyon, Section 629). In addition, a considerable number of synthetic fibers from protein materials (milk casein, fish protein, soy flour, etc.) have made their appearance. These protein fibers approach silk and wool in chemical composition, and they imitate the animal fibers in physical properties (insulating properties, absorption of dyes, etc.) as well. These important natural and synthetic protein materials will now be discussed.

**Silk.** The silkworm forms his cocoon by forcing *fibroin*, a protein, from two tiny openings under its mouth. As they emerge they are cemented together by a soluble protein, which is boiled off at some stage of the preparation of the silk goods. Silk is a durable, elastic fiber with an attractive luster. Its gossamer threads which delight the feminine, and masculine, eye attest its great tensile strength. Silk dissolves in sodium hydroxide and is more easily affected by acids than is wool.

**Wool.** Wool is made up of a complex protein called *keratin*, and is obtained from the fleeces of sheep, alpacas, goats, and similar animals. A strand of wool is seldom of uniform composition throughout its entire length. Three types of cells are present, and these overlap, like shingles, giving the fiber good felting qualities, high tensile strength, and enhanced elasticity. Alkalies easily dissolve it; in this respect it differs from cellulose fibers.

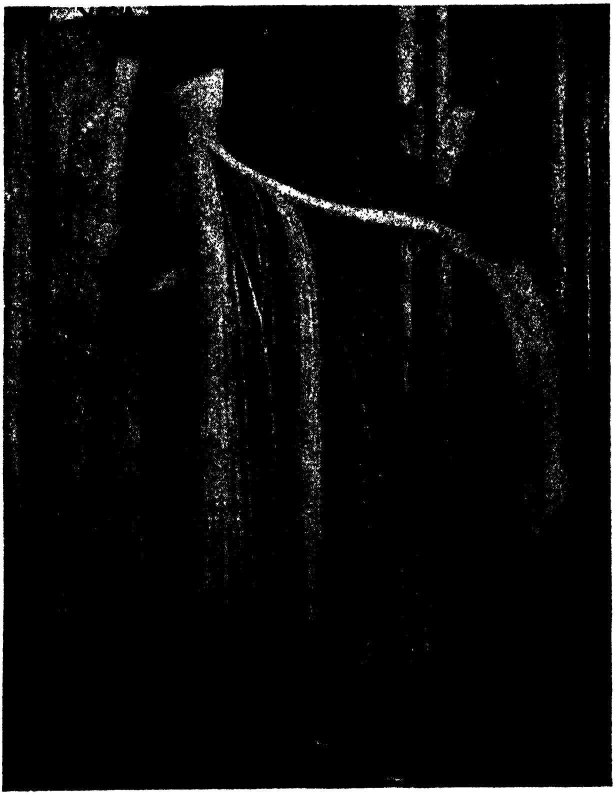
**Lanital.** When the British blockaded Italy during the invasion of Ethiopia, the supply of wool was curtailed. Italy met this challenge by producing a synthetic wool, **Lanital** (*lana*, meaning *wool*, and *Italia*) from the casein in skim milk. Since there are forty billion pounds of skim milk available for this purpose each year, sufficient raw material to produce a billion pounds of casein fiber, Lanital may some day rival rayon.

The manufacture is not unlike that used for rayon. Milk is centrifuged to remove the fatty matter from which butter is made. Buttermilk remains; this is heated and treated with sulfuric acid, precipitating the casein. The casein is dissolved in an alkali to which sodium aluminate is added. The solution is now aged at a constant temperature, polymerization taking place. Following this, the solution is ejected into an acid bath through spinerettes having 800 orifices, each 0.02 mm. in diameter. The fibers are united into a thread of any desired length, after which it is washed and dried.

Lanital has a natural crimp, like wool; in this respect it differs from most synthetic fibers. The chemical compositions of wool and Lanital are extremely alike, differing only as to sulfur content:

| | C | H | O | N | S |
|---|---|---|---|---|---|
| Wool | 49.25 | 7.57 | 23.66 | 15.86 | 3.66% |
| Lanital | 53 | 7 | 23 | 15.50 | 0.70% |

The disadvantage of Lanital, like the early rayons, is a poor tensile strength when wet. Despite this, the uniforms for the Italian army in 1940 contained



*Courtesy of the du Pont Company*

FIG. 221. Nylon, a material derived basically from coal, air and water, is shown in filaments of large diameters for surgical sutures, fishing leaders and brush bristles. A strand of this is many times the diameter of the fine yarn that goes into sheer nylon hosiery.

33 per cent Lanital woven with 67 per cent natural wool. In 1935 Italy produced its first pound of Lanital (Ferratti process); by 1939 annual production had swelled to 7,000,000 pounds, and similar processes were being perfected in Holland, England, the United States, and Japan.

Soybean and other protein fibers are also being developed.

**Nylon.** Based on posthumous patents by Wallace Carrothers, the du Pont Company in January 1940 offered a remarkable new material—**nylon**—for use in full-fashioned hosiery. Large plants have been built at Seaford, Del. and Martinsville, Va. for its production. The new fiber is completely synthetic ("coal, air and water"), and has a chemical composition not unlike the proteins in silk. It can be drawn to one-seventh the diameter of silk; its tensile strength is at least as good as silk; it is elastic, and is practically insensitive to moisture. High twist nylon yarn is being used for stockings and as a substitute for silk in parachutes; coarser fibers are for tooth-brushes (Fig. 221), fishing leaders, tennis racquet gut, dental floss, and surgical sutures. Nylon has assumed a vital rôle in war-time as a silk substitute.

This same material has been patented for transparent films for waterproofing paper and fabrics, for motion picture films in color-photography, as linings for containers, and as artificial patent leather.

Nylon fiber is made up of micelles formed by the condensation (organic combination, in which water is split off) of two straight-chain compounds, $NH_2-(CH_2)_x-NH_2$ and $COOH-(CH_2)_y-COOH$. The resulting material has the structure shown in Fig. 222. A great many of these units combine, since molecular

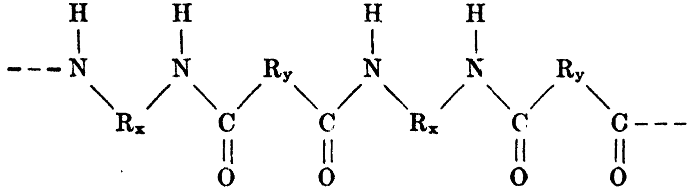


FIG. 222. Two nylon units.

weights exceed 20,000. Moreover the units may lie parallel to one another, or be cross-linked so as to intermingle; the nature of the linkage affects the properties of the final product.

The invention of nylon will have severe repercussions on the Japanese silk industry. Table 126 summarizes the various textile fibers produced during recent years. It is interesting to extrapolate these data into the future and to speculate upon their influence on international politics.

TABLE 126. WORLD PRODUCTION OF DIFFERENT TEXTILES
(1 = 100,000,000 pounds)

| Year | Cotton | Rayon | Wool | Lanital | Silk | Nylon |
|---|---|---|---|---|---|---|
| 1935 | 124 | 9.4 | 25 | start | 0.7 | — |
| 1938 | 126 | 9.9 | 25 | 0.07 | 0.7 | — |
| 1939 | 126 | 11.3 | 25 | 0.20 | 0.6 | start |
| 1942 (estimated) | | | | ? | ? | 0.15 |

## QUESTION REVIEW

### I. THE FOOD OF ANIMALS.

**Introductory** (656)

**a. Proteins** (657).

1. What instruments have recently been developed for studying the size and weight of protein molecules?
2. Give the structural formula for glycine, and show why it is called an amino-acid.
3. State three sources of proteins. Where does the vegetarian get his proteins?

**b. Carbohydrates and fats** (658).

4. Contrast fat with sugar as a source of body energy.
5. Devise some graphic presentation illustrating the food requirements of an average man.

**c. Mineral matter** (659).

6. What is the source of each of the following, and what foods supply them: calcium, phosphorus, iron, fats, carbohydrates, proteins?

**d. Vitamins** (660).

7. Compile a chart of the vitamins, their chemical names, the foods in which they are most abundant, and their biological actions.
8. Describe the research which precedes the marketing of some synthetic vitamin.
9. Give one interesting fact about each of the following: carotene, polished rice, night blindness, vitamin destroyed by cooking, rickets, cod-livers, the medical applications of vitamin $K_1$, the purpose of irradiating milk, the action of the fertility vitamin.

### II. ANIMAL PRODUCTS.

**a. Enzymes** (661).

10. Draw up a table showing the enzymes which will act on each of the following during its passage through the body: starch, fat, protein.

**b. Hormones** (662).

11. State the functions of five different hormones.
12. Draw the structural formula for theelin. For progesterone. For androsterone. (Formulas need not be memorized.)

**c. Protein fibers: silk, wool, Lanital, Nylon (663).**

13. Briefly summarize important facts about each of these four protein fibers.
14. Draw the chemical structure of a protein fiber. Of a cellulose fiber. In a few words indicate the differences in chemical composition. Contrast the properties of these two types of fibers.

**Reading References:** Articles in the Appendix:

*General:* 76, 257, 405, 406, 407, 415, 420 and 422.

*Strategic materials:* 133, 140, 142, 145, 151, 252, 326, 340, 345, 411, 412, 416 and 420.

*Textiles:* (*cellulose*): 14, 25, 110, 120, 125, 224, 250, 255, 311 and 333; (*protein*): 25, 80, 146, 220, 226, 250, 255 and 324.

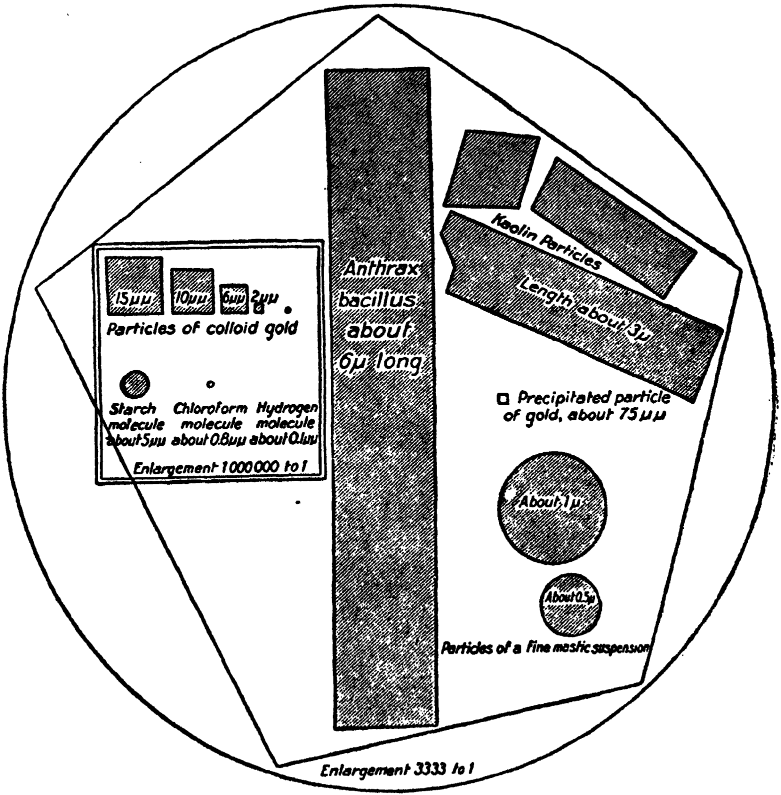
*Vitamins:* 232, 257 and 426.

# PART V: COLLOID CHEMISTRY

# CHAPTER XLVI

# COLLOID CHEMISTRY

**664. The Realm of Colloids.**—The student in qualitative analysis who has struggled to filter silver chloride (Dem. 55, Section 152) or some sulfide which persisted in passing through the filter paper, need hardly be advised of the existence of the colloidal state. These substances often persist in remaining in suspension, instead of precipitating as coarse particles. In this


15μμ
10μμ
6μμ
2μμ
Particles of colloid gold
Starch molecule about 5μμ
Chloroform molecule about 0.8μμ
Hydrogen molecule about 0.1μμ
Enlargement 1000000 to 1
Anthrax bacillus about 6μ long
Kaolin Particles
Length about 3μ
Precipitated particle of gold, about 75μμ
About 1μ
About 0.5μ
Particles of a fine mastic suspension
Enlargement 3333 to 1

*Courtesy, P. Blakiston's Son and Co.*

Fig. 223. Relative sizes of some particles.

respect, then, they differ from coarse suspensions or from substances in true solution.

Because molecular and colloidal forms of the same chemical substance differ strikingly in properties, the chemist has relegated the latter to a separate field of study: **colloid chemistry.** Arbitrarily this field is confined to particles larger than 1 millimicron and smaller than 100 millimicrons.* The lower limit corresponds to the size of our largest molecules (Fig. 223); while the upper limit is that which is barely visible in a powerful microscope.

These relationships are shown in Table 127.

TABLE 127. PROPERTIES IN THE COLLOID REGION COMPARED WITH PARTICLES OF OTHER SIZES

| Length of Particle | .1 mμ<br>1 Ångstrom | .001 μ<br>1 milli-micron | .01 μ | .1 μ | .001 mm.<br>1 micron | .01 mm. | .1 mm. | 1 mm.<br>1 milli-meter |
|---|---|---|---|---|---|---|---|---|
| SOLUTIONS | true molecular solutions | COLLOID SOLUTIONS | | | turbidities | coarse suspensions | | |
| (relative volumes) | mosquito | bee | | mouse | | | | elephant |
| DIALYSIS | pass through | NOT PASS THROUGH MEMBRANE | | | - - - - - - - - - - - - | | | |
| TYNDALL PHENOMENON | none | GIVES CONE OF LIGHT | | | opaque | | | |
| BROWNIAN MOVEMENT | tremendous | VERY FAST | | | slow - - - none at all - - - | | | |
| PREPARATION OF COLLOIDS | by CONDENSATION ——→ of smaller particles | | | | BY DISPERSION ←—— of larger particles | | | |
| | If a cube 1 mm. along each edge is subdivided into many small cubes, length of each as indicated above, the number of cubes and the area of their surface are as follows: | | | | | | | |
| NUMBER | — | — | $10^{16}$ | — | — | — | — | 1 cube |
| AREA | — | — | 600,000,000 sq. mm. | | | | — | 6 sq. mm. |

At one time it was thought that bodies were either **crystalline** or **colloidal.** Thomas Graham, who devised this classification, distinguished crystalline compounds such as salt, sugar, copper sulfate, and so forth, from gummy materials such as starch, glue, silicic acid and the like. The latter would not pass through the pores of animal membranes, since the molecules or clusters of molecules in solution were larger than the holes in the membrane. Experiment subsequently revealed, however, that all substances can be prepared in the colloidal state under appropriate conditions. Common salt, for example, crystallizes in the isometric system, but it is possible to disperse salt in petroleum ether so that it exhibits the colloidal state. A colloidal substance may therefore be crystalline. According to Bancroft, "we call any phase colloidal when it is sufficiently finely divided or dispersed. . . . Colloid chemistry is the chemistry of bubbles, drops, grains, filaments, and films, because in each of these cases at least one dimension of the phase is very small."

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* A millimicron is one-millionth of a millimeter; a micron is one-thousandth of a millimeter. Symbols: mμ, μ, mm.

Since any substance may be prepared as a colloid if its molecular aggregates are sufficiently large, the field of colloid chemistry is indeed vast. It may include mixtures of gases, liquids or solids (Table 128).

TABLE 128. THE DOMAIN OF COLLOIDS

| | |
|---|---|
| Gas in Liquid | Foams, beer froth. |
| Gas in Solid | Gaseous inclusions in minerals, metals; Ivory Soap (air beaten into soap). |
| Liquid in Gas | Fog, clouds. |
| Liquid in Liquid | Emulsions. |
| Liquid in Solid | Mercury ointments; liquid inclusions in rocks; jelly, gelatin. |
| Solid in Gas | Dust, comets, smoke. |
| Solid in Liquid | Sols. |
| Solid in Solid | Solid solutions, *e.g.*, colloidal selenium in ruby glass, coloring matter in gems. |

Colloid chemistry, then, is the chemistry of many of our important industrial products: milk, cream, butter and cheese; fog and mist; smoke and fine dust; froth and foam; cooking, washing, and dyeing materials; soap, greases, and oils; living matter; blood serum; the sap of plants; the principal articles of food; rubber, gums, clay, cements, ceramics; asphalt and plastics; roads; etc.

**665. Relative Sizes of Particles.**—The best microscope does not reveal particles having a diameter less than about 1/2,000 millimeter (0.5$\mu$). Colloidal particles are still smaller. In 1903, Siedentopf and Zsigmondy invented an instrument known as the **ultramicroscope,** which reveals particles having a diameter as small as 1/100,000 millimeter (10m$\mu$). This instrument involves the same principle as the Tyndall phenomenon (152). In the ultramicroscope a converging beam of intense light in a darkened room is sent horizontally through the liquid under examination and the scattered light is viewed from above, through an ordinary microscope. In the ultramicroscope, therefore, ultra-illumination is employed.

Since 1940 the scientist has been able with the help of the **electron microscope** (94) to probe still deeper into the realm of colloids. For though the ultramicroscope will reveal particles a little larger than 1000 Ångstroms in diameter, the electron microscope reveals particles down to 30 Ångstroms, that is, the region of the smallest of colloid particles. Interesting micrographs (Fig. 50) taken with the electron microscope indicate the size and shape of individual molecules of the tobacco-mosaic virus, and of single "grains" of silver in a photographic emulsion. Both of these particles are colloids.

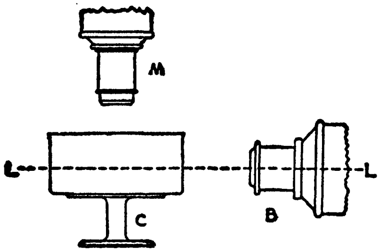


FIG. 224. Principle of the ultramicroscope. Ultra-illumination along *L–L* is passed through the colloidal solution *C*, the particles being observed from microscope, *M*.

### SOLS

**666. Preparation.**—Sols are particles of colloidal magnitude suspended in liquids. Referring to Table 127 it is evident that they may be prepared by aggregating single molecules (condensation methods) or by disintegrating coarse particles (dispersion methods).

**a. Condensation methods.**

DEMONSTRATION 164. PREPARATION OF SOLS BY CONDENSATION

Materials: Use distilled water throughout. (1) 1 per cent $AuCl_3$ solution; formaldehyde; 200 cc. water continuing 2cc. 1N $K_2CO_3$, rod. (2) Two 600-cc. beakers of water, one boiling; 1N $FeCl_3$; solution of $K_4Fe(CN)_6$. (3) 1 g. $As_2O_3$ in 100 cc. water heated to boiling, cooled and filtered; fresh $H_2S$-water, two 600 cc. beakers, filter paper in funnel. (4) Silver wires leading from 110 volts; 400-cc. beaker containing 0.01N NaOH.

(1) Colloidal gold may be prepared by adding three drops of 1 per cent gold chloride solution to 200 cc. of water containing formaldehyde, or other reducing agent. Colloidal gold of different colors, such as red, blue, and violet, may be prepared, the color depending more or less upon the size of the particles.

It is an interesting fact that Michael Faraday prepared violet and purple colloidal solutions of gold in 1857 by treating very dilute solutions of gold chloride with a solution of phosphorus in ether. Some of Faraday's specimens are preserved at the Royal Institution in London, one or two specimens still retaining a tinge of color, the rest having coagulated. Faraday's gold is an illustration of the preparation of a colloidal solution by chemical means.

(2) Reddish-brown ferric hydroxide sol is formed when a few drops of ferric chloride are added to the boiling water. If the water is cold, hydrolysis does not occur; no colloid is formed. This may be demonstrated by adding ferrocyanide: the ferric hydroxide sol gives no Prussian blue, whereas the solution containing $Fe^{+++}$ does.

(3) Colloidal arsenic trisulfide is prepared by the interaction of hydrogen sulfide and arsenious acid. The liquid should be a clear yellow, and pass readily through filter paper.

(4) When an arc is struck under water (**Bredig arc method**) between two metal wires (*e.g.*, silver, gold, platinum, palladium, iridium and cadmium) the metal disintegrates to form a vapor; this subsequently condenses into colloidal particles.

**b. Dispersion methods.**

(1) **Peptization** is the disintegration of a substance or body into colloidal particles by the action of an added agent, say, water or caustic soda. Thus, water is employed as a peptizing agent in "dissolving" gelatin or glue. As a matter of fact, these bodies do not form true solutions in water, but colloidal solutions. Again, silicic acid can be peptized by caustic soda.

In a similar manner colloidal solutions of glue, starch, and egg albumin may be prepared. Peptization is roughly analogous to digestion, in which pepsin plays a rôle.

(2) Colloidal nickel, tungsten, silica, etc., may be prepared by mechanical disintegration. **Colloid mills** (Fig. 226) for grinding, especially in making emulsions, accomplish the same purpose.

**667. Reversible and Irreversible Sols.**—Sols may be evaporated to dryness. If they coagulate so that they cannot be suspended again upon the addition of the dispersion liquid, they are called **irreversible sols.** Colloidal gold, silver, ferric hydroxide and the metallic sulfides belong in this category.

On the other hand, **emulsoids,** such as water suspensions of gelatin, glue, starch paste, egg albumin, etc., after evaporation to dryness, are readily thrown into suspension again by the addition of the dispersion means, *i.e.*, they are reversible.

**668. Properties of Colloids.**—The differences between true solutions and colloidal suspensions are emphasized in Table 127. A few of these differences will now be considered.

**a. Surface area.** A cube 1 inch along each edge has 6 square inches of surface. But if this same cube is broken down into nearly molecular dimensions, it will form at least $10^{18}$ cubes, and the area of the exposed material will be 5000 square feet. Obviously, properties which depend upon surface, such as catalytic activity, adsorption of dyes or gas, and relative reactivity, are enormously enhanced when the substance is reduced to the colloidal state.

**b. Dialysis.** Graham's original investigations showed that salts passed through an animal membrane whereas colloids did not. This property is utilized in purifying colloidal solutions: the sol is placed in a sac of collodion and suspended in a beaker of pure water (Fig. 74). Salts pass through the membrane and may be washed away, while the colloid particles remain in the sac. Graham called this **dialysis.**

Also, the size of the holes in the sac may be controlled by soaking the sac in alcohol-water mixtures. It is found that substances such as copper sulfate and sugar pass through small holes, but that gelatin, gold sols, ferric hydroxide sols, $K_4Fe(CN)_6$, etc. will only pass through large holes.

### DEMONSTRATION 165. DIFFUSION THROUGH GELATIN

Materials: (1) Tubes containing 1 per cent gelatin gel; solutions of colored salts; colored sols. (2) Large tube $\frac{3}{4}$ full of 2 per cent agar gel containing $K_4Fe(CN)_6$ and enough phenolphthalein to turn it pink. When the agar has set, fill the tube with dilute $FeCl_3$ solution.

The relative sizes of particles are revealed by the rate at which they diffuse through gelatin gels.

(1) If $CuSO_4$ solution is poured upon gelatin in one tube, and ferric hydroxide sol upon gelatin in the other, it will be found that the rate of diffusion of $Cu^{++}$ into the gelatin far exceeds that of the ferric hydroxide sol.

(2) The other experiment is known as the **patriotic test-tube.** $H^+$ and $Fe^{+++}$ start simultaneously to diffuse into the agar. The $H^+$ proceeds more rapidly, turning the pink phenolphthalein to white; the more slowly diffusing $Fe^{+++}$ forms a Prussian blue zone of $Fe_4[Fe(CN)_6]_3$. In a few days the contents of the tube are red (bottom), white and blue (top).

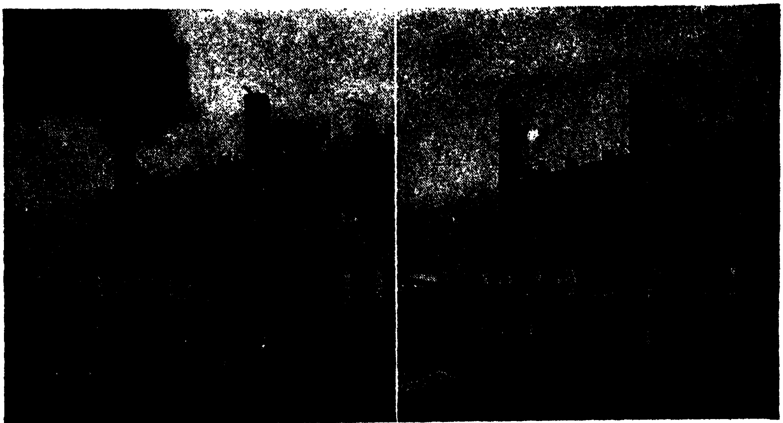
**c. Tyndall Phenomenon.** When a strong light is passed through a colloidal suspension, a cone of light scattered by the dispersed particles reveals the colloidal state. This is what we see in the beam from an automobile headlight during a fog. True solutions, with the exception of certain heavy metal salts (*e.g.* $NiSO_4$), do not reveal this Tyndall cone.

**d. Brownian Movement.** Colloidal solutions exhibit the Brownian movement, but true solutions do not. The particles of the colloid are suspended in the dispersion means (ordinarily water), and are subjected to lively bombardment by the molecules of the liquid, and are thus kept in a state of perpetual motion. When viewed through the ultramicroscope, this phenomenon is most interesting. The colloidal particles are not actually visible, but one sees the light diffracted by them. This phenomenon may be compared to motes dancing in a beam of sunlight. See Fig. 52.

**669. Electrical Properties of Sols.**—Colloid particles adsorb large numbers of ions on their surfaces and accordingly become electrically charged. Metals and metallic sulfides adsorb negative ions; they are **negative sols** which move towards the anode when an electric current is passed through them. Sols of metallic oxides adsorb positive ions, and are therefore called **positive sols**; they migrate to the cathode in an electric field.

**a. Electrodeposition.** This property is made use of in electroplating rubber; the rubber colloid is negative, and if the metal anode is fashioned in the shape of a hand, the rubber particles migrate to it and are deposited upon it in the form of a rubber glove. Numerous other miscellaneous articles may be manufactured by electrodeposition in this way.

**b. Precipitation by electrolytes.** If the charge on the colloid particle is neutralized by adding an electrolyte, the particles agglomerate and precipitation occurs.



*Courtesy of the Western Precipitation Corporation*

FIG. 225. Cottrell precipitator. *Left:* off. *Right:* on. Used in the control of dusts and fumes; and in the recovery of valuable ores from these dusts.

Milk casein is precipitated by $H_2SO_4$ in making lanital (synthetic wool, **663**). Another example of precipitation by electrolytes is in the colloidal clay which is carried thousands of miles by the waters of great rivers, but is deposited as a delta when it encounters the salt of the sea. Another interesting application is to the precipitation of dust and smoke. F. G. Cottrell, an American chemist, perfected an industrial method which is called the **Cottrell process.** It is employed, for instance, in smelting-works, in cement-mills, and in sulfuric acid plants. The colloidal particles are precipitated by means of electrical forces. The dust or smoke is made to pass wires or rods charged to about 70,000 volts and suspended in the center of a chimney or dust chamber. The particles take on a charge similar to that of the rods, whereupon they are attracted to a pipe or curtain of rods, placed three to six inches from the charging electrodes. The dust is thereby precipitated. Ofttimes this flue dust is so valuable that the profits of a company depend upon its recovery and subsequent treatment (Fig. 225).

**c. Mutual precipitation of colloids.** If two colloids of opposite charge are mixed, they mutually precipitate one another.

### DEMONSTRATION 166. PRECIPITATION OF COLLOIDS

Materials: Colloidal $As_2S_3$; colloidal $Fe(OH)_3$; 3 test-glasses.

When a colloidal solution of arsenic trisulfide (negative) is mixed with one of ferric hydroxide (positive), precipitation occurs, for the oppositely charged particles neutralize one another.

**d. Protective colloids.** Settling may be prevented by the presence of protecting films. When Faraday prepared colloidal gold in 1857 he observed that a little jelly kept his preparations from coagulating. The action of gelatin in preventing coagulation is of much interest and importance.

Materials: 400-cc. beakers of water over burners, one containing a few cc. of 1 per cent gelatin solution; 0.1N $AgNO_3$; 1N $K_2Cr_2O_7$.

If a few cc. of silver nitrate and of potassium dichromate are poured into boiling water, a curdy precipitate of silver chromate is obtained. If, however, a few cc. of gelatin is previously added to the water, a colloidal suspension is formed instead.

The gelatin covers the solid suspensoid particles, thus preventing their coming together to form larger aggregates. Such organic colloids as gelatin and the proteins increase the stability of colloidal metals; hence they are termed **protective colloids.**

Colloidal silver chloride, bromide and iodide may also be prepared. The emulsions of the halides of silver are of great importance in photography.

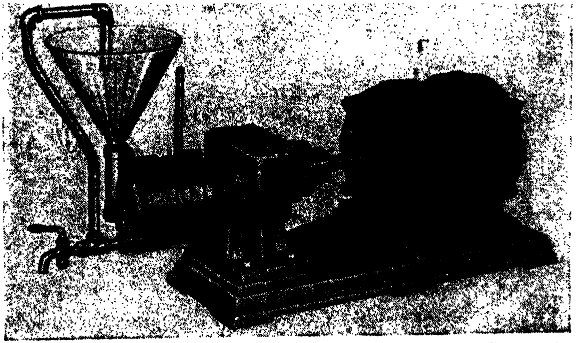
### DEMONSTRATION 168. STABILIZING FOAM

Materials: Ten grams of albumin-free baking powder (*e.g.*, Royal) in 2 test-glasses; egg albumin.

If water is added to baking powder containing 1/2 g. of egg albumin a permanent foam is formed. The albuminous material coats the bubbles of carbon dioxide which are formed. In baking, flour supplies the albumin. This experiment also illustrates another important industrial application of colloid chemistry.

## EMULSIONS

**670. Emulsions.**—An **emulsion** consists of droplets of one liquid suspended in another. It is easy to prepare emulsions by shaking two immiscible liquids together: *e.g.*, water and kerosene. Such dispersions, however, are temporary, the emulsions quickly separating into their components. In order to preserve an emulsion, it is necessary to have present a third substance—an **emulsifying agent.** Mayonnaise dressing, for example, is an emulsion of vinegar and olive oil, with the yolk of an egg as emulsifying agent.



*Courtesy of U. S. Colloid Mill Corporation*

FIG. 226. A colloid mill.

### DEMONSTRATION 169. FORMATION OF AN EMULSION

Materials: (*a*) Two 200-cc. stoppered cylinders half-full of water; soap solution; kerosene. (*b*) Solution of rosin in alcohol in stoppered cylinder; water.

(*a*) Although kerosene and water mix only temporarily, a permanent emulsion may be formed by the addition of soap solution as the emulsifying agent.

(*b*) Again, rosin emulsifies water and alcohol.

The **colloid mill** (Fig. 226) is particularly useful for preparing fine emulsions. It consists of two rapidly whirling surfaces which disperse the coarse particles very effectively.

## GELS

**671. Gels.**—When the colloidal system sets to a more or less solid form it is called a gel.

### DEMONSTRATION 170. FORMATION OF A GEL

Materials: (*a*) Ten cubic centimeters of saturated calcium acetate, 90 cc. of 95 per cent ethyl alcohol, 2 beakers. (*b*) 600 cc. beaker containing 6 per cent HCl; 200 cc. of sodium silicate of sp.gr. 1.2.

(*a*) Upon mixing calcium acetate and alcohol in the proper proportions, a solid gel of alcohol is obtained. The gel may be ignited, for it is similar to "canned heat" (*e.g.*, Sterno).

(*b*) When sodium silicate is poured into hydrochloric acid, a white mass is formed; it is known as **silica gel.** It will not form if 10 per cent acid is poured into sodium silicate of sp. gr. 1.185, showing that the conditions of mixing may determine the extent of aggregation of the product. Silica gel is of great industrial importance as a catalyst support and absorbent for vapors and liquids. The term gel includes jelly, such as fruit jelly. Sometimes there is difficulty in getting the jelly properly to form, but coalescence and agglomeration can be induced by the addition of **pectin,** a preparation which may be purchased. Pectin is present in ripe fruits, and the jellying of fruit-juices depends upon it. If the fruit is cooked too much, pectin is converted into other substances and the formation of jelly is prevented.

## QUESTION REVIEW

I. INTRODUCTION.

**a. The realm of colloids (664).**

1. How many microns are there in 1 kilometer? How many Ångstroms in 1 millimicron? In terms of millimeters, what are the boundaries of the colloid state?
2. Give an example of each of the eight classes of colloids (gas in liquid, gas in solid, etc.).

**b. Relative sizes of particles (665).**

3. Compare the region of colloid chemistry invaded by the electron microscope with that possible with an ordinary microscope. With that of an ultra-microscope.

II. SOLS.

**a. Preparation (666).**

4. Give two specific examples of sols prepared by condensation methods. Two of sols prepared by dispersion methods.

**b. Reversible and irreversible sols (667).**

**c. Properties of colloids (668).**

5. Explain four properties of colloids which distinguish them from true solutions and coarse suspensions.

**d. Electrical properties of sols (669).**

6. Explain four types of phenomena connected with the electrical charge on colloidal particles.
7. Explain each of the following: stabilizing foam, reversible sol, colloid mill, Bredig arc, mutual precipitation of colloids, protective colloids, Tyndall cone, dialysis, ultracentrifuge.
8. Explain, with equations, the patriotic test-tube experiment.

III. EMULSIONS (670).

9. Explain what is meant by an emulsifying agent. Illustrate.

IV. GELS (671).

10. Describe how two gels may be prepared in the laboratory.

**Reading References:** Articles number 2, 6, 42, 67, 79, 208, 306, 332 and 406.

## PROBLEMS

### PERCENTAGE COMPOSITION (107)

1. Calculate the percentage composition of lead nitrate, calcium phosphate limonite ($2Fe_2O_3, 3H_2O$), Paris green ($Cu(C_2H_3O_2)_2, Cu_3(AsO_3)_2$) and calcium, bicarbonate ($Ca(HCO_3)_2$).

2. Calculate the percentage composition of ordinary alum ($K_2Al_2(SO_4)_4, 24H_2O$) and of potassium ferrocyanide ($K_4Fe(CN)_6, 3H_2O$).

3. Calculate the percentage composition of gypsum ($CaSO_4, 2H_2O$).

4. Calculate the percentage of water in crystallized copper sulfate or blue vitriol ($CuSO_4, 5H_2O$).

5. Calculate the percentage of copper in the mineral azurite ($Cu(OH)_2, 2CuCO_3$). *Ans.* 55.34 per cent.

6. Find the percentage of silver in $NaAg(CN)_2$, and of uranium and vanadium in carnotite ($K_2O, 2UO_3, V_2O_5, 3H_2O$).

7. Find the percentage of copper in the mineral enargite ($3Cu_2S, As_2S_5$).

8. Find the percentage of $SiO_2$ in talc ($Mg_3H_2(SiO_3)_4$) and of $Al_2O_3$ in kaolinite ($Al_2H_2(SiO_4)_2, H_2O$).

9. Find the percentage composition of feldspar ($KAlSi_3O_8$) expressed as $K_2O$, $Al_2O_3$, and $SiO_2$.

10. Calculate the percentage of phosphorus in apatite ($Ca_4(CaF)\ (PO_4)_3$).

### FORMULAE, AND EQUIVALENT WEIGHTS (105, 108)

11. A specimen of the mineral chalcopyrite yielded on analysis 34.40 per cent of copper, 30.47 per cent of iron, and 35.87 per cent of sulfur. Derive its empirical formula.

12. 2.6 g. of mercurous oxide was heated, and yielded 0.1 g. of oxygen. Find the simplest formula of the compound and the equivalent weight of mercury in this oxide.

13. A compound on analysis yielded 22.77 per cent of sodium, 21.78 per cent of boron, and 55.45 per cent of oxygen. Calculate its simplest formula.

14. 2.238 g. of pure iron combined with oxygen to form 3.198 g. of dried rust. Find the equivalent weight of iron and the simplest formula for this oxide of iron.

15. A compound contains 26.53 per cent of potassium, 35.37 of chromium, and 38.10 of oxygen. Find its simplest formula.

16. Derive the empirical formula of mercuric cyanide, 10.8 g. of which lost 2.2 g. of cyanogen upon heating.

17. Find the formula of the hydrate aluminum sulfate, 4.77 g. of which lost 2.305 g. of water when heated to constant weight.

18. Analysis shows that a certain compound contains the following percentages: calcium oxide, 1.90; alumina, 37.72; silica, 23.53; water, 36.85. Find its empirical formula.

19. 3.167 g. of aluminum hydroxide lost 1.0933 g. of water when heated to constant weight. Find its simplest formula.

20. A silicate of calcium and magnesium contains the following percentages: calcium, 8.32; magnesium, 15.16; silicon, 23.29; oxygen, 53.23. Find its simplest formula.

21. Find the simplest formula of the substance having the following composition: K, 8.24; Al, 5.69; S, 13.50; O, 27.01; $H_2O$, 45.56.

22. Assign a formula to the substance which, by analysis, yielded the following percentage composition: $Al_2O_3$, 16.86; CaO, 9.20; $SiO_2$, 59.28; $H_2O$, 14.66.

23. Three oxides of nitrogen contain, respectively, the following percentages of nitrogen: 63.65, 46.68, and 36.86. Find the equivalent of nitrogen in each compound.

24. 1.665 g. of lead chloride yielded 1.778 g. of silver chloride. What is the equivalent of lead?

25. If 2.1765 g. potassium bromide required, for complete precipitation, 1.993 g. of pure silver dissolved in nitric acid, what is the equivalent of bromine?

## THE EFFECT OF PRESSURE AND TEMPERATURE UPON GASES (75–84)

26. 25 cc. of hydrogen was collected under a pressure of 720 mm. What is its volume at 760 mm.?

27. 42 cc. of gas was collected under a pressure of 800 mm. What is the volume at 760 mm.?

28. 100 cc. of hydrogen at 760 mm. is compressed until its volume is 85 cc. What is the new pressure?

29. 10.5 cc. of a gas at 21° C. will occupy what volume at 0° C.?

30. 30 cc. of oxygen are at 16° C. What would the volume be at 55° F.? *Ans.* 29.67 cc.

31. 25 cc. of a gas was collected at 20° C. and under a pressure of 750 mm. What is the volume under standard conditions? *Ans.* 22.99 cc.

32. 23.4 cc. of air is measured at −10° F. and 730 mm. What will the volume be at 0° C. and 760 mm.? *Ans.* 24.58 cc.

33. 34.6 cc. of hydrogen is collected at 17° C. and under pressure of 780 mm. What is the volume at 75° F. and 750 mm.? *Ans.* 36.84 cc.

34. How many grams of potassium chlorate is required to prepare a liter of oxygen at 22° C. with the barometer at 765 mm. *Ans.* 3.398 g.

35. The result of a calculation gave 22.4 cc. of a gas at 0° C. and 760 mm. The gas was collected at 20° C. and 770 mm. What was the observed volume, and what was the weight of the gas, if a liter of it, at standard conditions, weighs 1.430 g.? *Ans.* 23.73 cc.
0.03203 g.

36. Suppose we have 250 cc. of nitrogen at 60° F. and 730 mm. pressure, what will the volume be if the temperature becomes 30° C. and the pressure 780 mm.? *Ans.* 245.6 cc.

37. Reduce 60 cc. of oxygen, measured over water at 20° C. and 763 mm. to the *dry* condition and to 0° C. and 760 mm.

38. The result of a calculation gave 3.55 liters of hydrogen at S.T.P. The gas was collected over water at 18° and under a pressure of 763 mm. What was the observed volume? *Ans.* 3.85 liters.

39. 100 cc. of hydrogen at 20° and 756 mm. will have what volume at −10° and 761 mm.? *Ans.* 89.16 cc.

40. The result of a calculation gave 22,400 cc. of a pure, dry gas at 0° and 760 mm. The gas was collected over water at 25° and 755 mm. Find the observed volume of the gas and the weight, if a liter of the dry gas at 0° and 760 mm. weighs 1.251 g. *Ans.* 25,405 cc.
28.022 g.

41. One liter of oxygen, at S.T.P., weighs 1.429 g. 350 cc. of this gas measured over water at 22° and 753 mm. will contain what weight of the dry gas? *Ans.* 0.4467 g.

42. What is the absolute density of air at 21° and 762 mm.? of hydrogen at −10° and 745 mm.? *Ans.* Density of air = 0.001204.
Density of hydrogen = 0.0000916.

43. The density of a substance referred to air is 2.21. What is its density referred to oxygen and to hydrogen, and what volume would 2 g. of the substance occupy at 21° and 765 mm.?

*Ans.* Density referred to oxygen = 1.999.
Density referred to hydrogen = 31.82.
Volume = 750.2 cc.

44. Reduce 60 cc. of gas at 21° C. and 740 mm. to 21° F. and 755 mm. *Ans.* 55.85 cc.

45. A flask while open to the air is heated to 100° C., the barometric pressure being 766 mm. It is then closed and allowed to cool at 22° C. Find the final pressure. *Ans.* 605.8 mm.

46. A quantity of oxygen has a volume of 40 cc. at 27° C. At what temperature would its volume become 30 cc.? *Ans.* −48° C.

47. A quantity of air having a volume of 125 cc. and a pressure of 755 mm. is expanded, the temperature being kept constant, to a volume of 625 cc. Find the final pressure. *Ans.* 151 mm.

48. A flask is filled with air at −10° F. and 755 mm. If the barometric pressure remains constant, to what temperature must the flask be raised to drive out half of the air that was in it when it was filled? *Ans.* 226.3° C.

49. A volume of nitrogen in a tube over mercury measured 60 cc. The mercury in the tube was 50 mm. above the surface of the mercury in the trough, and the barometric pressure was 755 mm. What would have been the volume if exposed to the standard pressure alone? What would be the volume of nitrogen if the tube were forced down until the mercury in the tube is 50 mm. below the surface of the mercury in the trough?

*Ans.* 55.66 cc.
52.54 cc.

50. One liter of oxygen, at S.T.P., weighs 1.429 g. What weight of the gas is contained at 20° C. in a tank having a capacity of 2.5 liters, the pressure being 10 atmospheres? *Ans.* 33.29 g.

51. The density of a certain gas is .001204 at 21° C. and 762 mm. Find the weight of a liter of the gas at S.T.P.

52. A glass bottle is capable of standing a pressure of 3 atmospheres. If the bottle be filled with oxygen at −10° C. and 760 mm., to what temperature should the gas be heated to burst the bottle?

## WEIGHT AND VOLUME (109–111)

53. What volume of oxygen, measured at 20° and 745 mm., can be obtained by strongly heating 7 g. of potassium chlorate?

54. How many grams of each of the following substances would have to be heated to obtain 3 liters of oxygen: (*a*) Mercuric oxide, (*b*) manganese dioxide, (*c*) barium peroxide?

*Ans.* (*a*) 58.01 g. HgO.
(*b*) 34.93 g. $MnO_2$.
(*c*) 45.37 g. $BaO_2$.

55. What volume of chlorine gas could be obtained from 200 g. of sodium chloride? What volume of hydrogen chloride could be obtained by allowing this volume of chlorine to unite with hydrogen?

*Ans.* 38.32 liters of chlorine.

56. A quantity of carbon monoxide was passed through a red-hot tube containing ferric oxide. The resulting gas was absorbed by caustic potash, the gain in weight being 1 g. What volume of carbon monoxide at S.T.P. was required? *Ans.* 0.507 liter.

57. A certain weight of potassium chlorate was heated until completely decomposed, and the residue weighed 24.62 g. What weight of potassium chlorate was heated, and what weight of oxygen was obtained?

*Ans.* 40.47 g. $KClO_3$.
15.85 g. $O_2$.

58. How many grams of sulfuric acid containing 16 per cent of $H_2SO_4$ will it take to dissolve 100 g. of zinc? *Ans.* 936.5 g.

59. How many grams of hydrogen will be liberated when 40 g. of zinc alloy containing 10 per cent of magnesium are dissolved by hydrochloric acid? How many grams of acid will be used up, and how much zinc and magnesium chloride will be formed? *Ans.* 1.43 g. $H_2$.
52.17 g. HCl.
75.08 g. $ZnCl_2$.
15.68 g. $MgCl_2$.

60. What weight of sulfuric acid containing 12 per cent of $H_2SO_4$ will dissolve 5 g. of iron wire 99.6 per cent pure? *Ans.* 72.89 g.

61. How many kilograms of sodium chloride is necessary to prepare 60 kilograms of hydrochloric acid containing 25 per cent of available acid? *Ans.* 24.04 kg.

62. What weight of magnesium would be required to generate hydrogen enough to fill a balloon with a capacity of 20 liters, at 22° and 775 mm.? *Ans.* 20.48 g.

63. What volume of hydrogen measured over water at 21° and 750 mm. will be liberated when 20 g. of an alloy containing 90 per cent of zinc and 10 per cent of magnesium are dissolved in hydrochloric acid?

64. How much chlorine by weight and by volume (S.T.P.) can be obtained from 75 g. of pure salt? What volume would the gas occupy at 10° and 735 mm.? *Ans.* 45.52 g.
14.36 liters.
15.39 liters.

65. How many grams of iron are required completely to reduce 10 liters of water vapor measured at 130° and 745 mm.? *Ans.* 12.41 g.

66. If the density of sulfur dioxide under certain conditions is 0.003, what volume of the gas would be produced, under these conditions, by burning 12 g. of sulfur?

67. (*a*) What volume of nitrogen at 20° and 770 mm. can be obtained by heating 33 g. of ammonium nitrite? (*b*) What volume would the gas occupy at 65° F. and 745 mm.? *Ans.* (*a*) 12.23 liters.
(*b*) 12.57 liters.

68. How large a tank could be filled with acetylene gas, at 21° and 765 mm., by decomposing 100 kilograms of calcium carbide with water? *Ans.* 37,450 liters.

69. The formula of gypsum is $CaSO_4, 2H_2O$. What volume of water vapor, at 300° C. and 750 mm., would be liberated by heating 172 g. of gypsum? *Ans.* 95.28 liters.

70. A specimen of iron pyrites was found on analysis to contain 50 per cent of sulfur. Suppose that all the sulfur in 5 kilos. of the mineral is oxidized to sulfur dioxide, what are the weights and volumes of the gases at 25° and 110 mm.? *Ans.* 5 kg. $SO_2$ and 2.5 kg. $O_2$.
13,200 liters.

71. Ten grams of an alloy of zinc and magnesium (containing 10 per cent Mg.) was placed in a flask containing 90 g. of sulfuric acid (25 per cent $H_2SO_4$). What weight and volume of hydrogen were liberated? *Ans.* 0.3575 g.
3.977 liters.

72. How many cubic centimeters of carbon dioxide, measured at 20° and 745 mm., will be absorbed by a solution containing 3 g. of sodium hydroxide, to form sodium carbonate? *Ans.* 919.4 cc.

73. A sample of Epsom salt ($MgSO_4, 7H_2O$), after heating until it became anhydrous, left a residue weighing 4 g. Find the weight of the original sample, and the volume which the water would occupy at S.T.P.

74. What volume of hydrogen sulfide (S.T.P.) is needed to reduce 2.4 g. of potassium permanganate in sulfuric acid solution?

75. What volume of methane, measured over water at 20° and 765 mm., could be obtained by heating 5.25 g. of anhydrous sodium acetate with excess of soda-lime? What volume of pure oxygen (S.T.P.) would be required completely to burn the methane?

76. Assuming that the temperature and pressure are constant, what volume of gaseous product may be obtained by exploding a mixture of 125 cc. of carbon monoxide and 60 cc. of oxygen?

77. A mixture of 150 cc. of methane and 75 cc. of oxygen was exploded by means of an electric spark. Find the volume of the product after the removal of aqueous vapor by absorption in phosphoric anhydride, assuming that the temperature is 100° C. and the pressure 760 mm. throughout.

78. 100 cc. of a mixture of nitrogen and methane was exploded with 200 cc. of oxygen. The volume of the *dry* gaseous product was found to be 250 cc. Find the percentage of methane in the original sample, assuming that the pressure and temperature are constant throughout.

*Ans.* 25 per cent.

79. If a paraffin candle (C 85 per cent, H 15 per cent) loses 40 g. by burning, find the weights and volumes of the products of combustion and of the oxygen used, assuming that the pressure is 770 mm. and the temperature 102°.

*Ans.* 54 g. and 91.1 liters $H_2O$.
124.67 g. and 86 liters $CO_2$.
138.67 g. and 131.5 liters $O_2$.

80. Sodium peroxide, when added to water, liberates 3.5 liters of oxygen when collected over water at 21° and 763 mm. Find the weight of peroxide decomposed and the weight of sodium hydroxide formed.

*Ans.* 22.18 g. $Na_2O_2$.
22.75 g. NaOH.

81. A sample of water glass weighing 1.189 g. yielded upon analysis 0.072 g. of $SiO_2$ and 0.2307 g. of a mixture of NaCl and KCl. From the mixed chlorides 0.0687 g. of $K_2PtCl_6$ was obtained. Calculate the percentages of $Na_2O$, $K_2O$, and $SiO_2$ contained in the sample analyzed.

*Ans.* 6.06 per cent $SiO_2$.
9.38 per cent $Na_2O$.
1.12 per cent $K_2O$.

82. If 1 g. of water at 20° absorbs 0.526 g. of ammonia gas, how much ammonium sulfate would be required to prepare enough of the gas to saturate 1,000 g. of water at 20°? What volume would the gas occupy if measured dry at 22° and 745 mm.?

83. (*a*) What weight of quartz sand should be necessary to flux the lime contained in 1 kilogram of limestone containing 85 per cent of calcium carbonate?

(*b*) What volume of carbon dioxide, measured at 25° and 765 mm., should be produced?

84. A dilute solution of sulfuric acid was electrolyzed and the evolved gases collected above the electrodes. What were the volumes occupied by the moist hydrogen and oxygen when 0.03 g. of water had been decomposed, the temperature being 23° and the pressure 775 mm.?

## MOLECULAR FORMULAE, MOLECULAR WEIGHTS, AND ATOMIC WEIGHTS (114–124)

85. A compound contains 17.647 per cent of hydrogen and 82.353 per cent of nitrogen, and its specific gravity (air = 1) is 0.5886. What is the formula of the compound?

86. A compound contains 85.71 per cent of carbon and 14.29 per cent of hydrogen, and its sp. gr. (air = 1) is 0.97. What is its formula?

87. The weight of 1 liter of gas at 0° and 760 mm. is 5.236 g. What is its density referred to air and to hydrogen, and what is its molecular weight?

88. The weight of 1 liter of gas at 0° and 760 mm. is 1.628. What is the molecular weight of the gas?

89. 111.4 cc. of a gas at 27° and 750 mm. weigh 0.1537 g. What is its molecular weight?

90. If the vapor density of phosphorus is 4.3 (air = 1) and its atomic weight 31, what is its molecular weight? What is its molecular formula?

91. The specific gravity of sulfur dioxide (oxygen = 1) is 2.002. What is its molecular weight?

92. 8,019 cc. of a gas collected at 20° and 742.4 mm. pressure weighed 14 g. What is its molecular weight? *Ans.* 42.96.

93. From the following data find the atomic weight of chlorine and assign formulae to the compounds. (Atomic weights: O = 16, C = 12, H = 1.008, P = 31.)

| Compounds | Weight 22.4 L | Weight Hydrogen | Weight Chlorine | Weight Carbon | Weight Oxygen | Weight Phosphorus |
|---|---|---|---|---|---|---|
| Hydrogen chloride | 36.468 | 1.008 | 35.46 | .. | .. | .. |
| Phosgene | 98.92 | .. | 70.92 | 12 | 16 | .. |
| Phosphorus trichloride | 137.38 | .. | 106.38 | .. | .. | 31 |
| Phosphorus oxychloride | 153.38 | .. | 106.38 | .. | 16 | 31 |
| Chlorine dioxide | 67.46 | .. | 35.46 | .. | 32 | .. |
| Chloroform | 119.388 | 1.008 | 106.38 | 12 | .. | .. |
| Carbon tetrachloride | 153.84 | .. | 141.84 | 12 | .. | .. |

94. The weight of 1 liter, at S.T.P., of each of several elementary substances is as follows:

| | |
|---|---|
| Hydrogen | 0.08987 g. |
| Oxygen | 1.429 " |
| Nitrogen | 1.2507 " |
| Chlorine | 3.22 " |
| Mercury (vapor) | 8.87 " |
| Ozone | 2.14 " |

Find the molecular weight and select the molecular formula of each substance.

95. If the specific heat of zinc is 0.094 and the equivalent weight is 32.7, what is its exact atomic weight?

96. Platinic chloride contains 57.92 per cent of platinum and 42.08 per cent of chlorine. The specific heat of platinum is 0.0324; calculate (*a*) the exact atomic weight of platinum and (*b*) the formula of platinic chloride.

97. 44.5274 g. of NaCl was dissolved in water and treated with silver nitrate. The pure silver chloride obtained weighed 109.1897 g. Taking the atomic weight of silver as 107.88 and that of chlorine as 35.46, find the atomic weight of sodium.

98. Derive the formula of the hydrate Glauber's salt, 8.16 g. of which lost 4.51 g. of water upon heating.

99. 2.3737 g. of gypsum was heated to constant weight, which was found to be 1.8768 g. Find the formula of gypsum, assuming the formula of calcium sulfate to be $CaSO_4$.

100. Assign a formula to the substance which, by analysis, yielded the following percentage composition: $Al_2O_3$, 16.86, CaO, 9.20, $SiO_2$, 59.28, $H_2O$, 14.66.

101. According to Stas, 53.1958 g. of silver form 92.6042 g. of silver bromide. Calculate the atomic weight of silver, given the atomic weight of bromine as 79.92.

102. A carbon compound by analysis yielded the following percentages: C 30.45, H 3.83, Cl 45.69, O 20.23. The specific gravity of its vapor referred to air was found to be 5.48. Find the formula of the compound.

103. The freezing point of a 3.3 per cent solution of hydrogen peroxide in water was found to be −2.03° C. Calculate the depression produced by 3.3 g. of hydrogen peroxide in 1,000 g. of water, and from the value thus obtained find out the weight of hydrogen peroxide required to produce a depression of 1.86° C. in 1,000 g. of water, and then assign the formula to the compound. *Ans.* −0.196° C.
31.3.

104. If 5 g. of a substance, dissolved in 1,000 g. of water, gave a solution freezing at −0.2° C., what is the molecular weight of the substance?
*Ans.* 47.

105. An automobile anti-freeze solution is prepared by mixing equal weights of glycerine ($C_3H_5(OH)_3$) and water. What is the calculated freezing point of this solution on (*a*) the Centigrade scale; (*b*) the Fahrenheit scale?

106. According to experiments of Marignac, 5 g. of strontium chloride, containing 6 molecules of water of hydration, yielded 3.442 g. of strontium sulfate. Find the equivalent weight of strontium.

107. A liter of oxygen weighs 1.429 g. A liter of the gas of a certain gaseous element, the molecules of which are diatomic, weighs 1.2507 g. Find the atomic weight of the element.

108. The analysis of a compound containing carbon, hydrogen, nitrogen, and oxygen yielded the following results: 0.2169 g. of the substance, when oxidized, gave 0.517 g. of $CO_2$ and 0.0685 g. of $H_2O$. 0.2218 g. of the compound, when decomposed, gave 17.4 cc. of nitrogen, measured over water at 6° C., and 762 mm. First find the percentage composition of the compound and then its simplest formula.

## Normal Solutions and Equivalent Weights (160–162)

109. (*a*) Calculate the number of grams of each of the most important bases and acids required to prepare a liter of a normal solution; also a liter of a molar solution.

(*b*) In making up one liter of each of the following, state how much of the solute indicated you would have to weigh out: (*a*) 0.5 normal $Na_2SO_4$; (*b*) 2-normal $CuSO_4, 5H_2O$; (*c*) 0.1 normal $Al_2(SO_4)_3$; (*d*) molar $Na_3PO_4$; 0.1 normal $BaCl_2$.

110. (*a*) 20 cc. of normal sulfuric acid is used to neutralize a solution of sodium carbonate. How many equivalents of sodium carbonate were in the solution? How many grams of sodium carbonate?

(*b*) Repeat the problem using sodium hydrogen carbonate in place of sodium carbonate.

111. How many equivalents of chlorine are precipitated by 20 cc. of a normal solution of silver nitrate? How many grams of silver and of chlorine are present in the precipitate?

112. If the bromine in 15 g. of potassium bromide be liberated in 5.5 liters of solution, find the concentration of the solution in equivalents and in grams.
*Ans.* 0.023 equiv.
1.833 g. of bromine per liter.

113. If 35.5 cc. of normal potassium hydroxide is required to neutralize 25 cc. of sulfuric acid, what is the normality of the acid?

114. What volume of $N/5$ hydrochloric acid would be required to decompose 120 cc. of $N/2$ sodium bicarbonate?

115. (*a*) What volume of normal sulfuric acid can be neutralized by 15 g. of washing soda ($Na_2CO_3 . 10H_2O$?)

(*b*) One gram of baking soda, dissolved in water, required 10 cc. of normal acid to neutralize it. What per cent of sodium bicarbonate did the soda contain? *Ans.* (*a*) 104.9 cc. acid.
(*b*) 84 per cent of $NaHCO_3$.

116. What weight of chlorine is present per cc. of *N*/10 calcium chloride solution? What weight of silver nitrate would be required to combine with the chloride present in 16 cc. of the solution?
*Ans.* 0.00355 g. of chlorine.
0.272 g. of $AgNO_3$.

117. How many cc. of *N*/10 chlorine water must be added to a solution containing 1.3 g. of potassium iodide in order to set free all the iodine?
*Ans.* 78.3 cc.

118. An excess of ferrous sulfide was added to 80 cc. of a dilute sulfuric acid and the volume of $H_2S$ set free measured 650 cc. at S.T.P. Calculate the normality of the acid. *Ans.* 0.725 *N*.

119. What volume of hydrogen at S.T.P. should be obtained by treating 35 cc. of *N*/2 sulfuric acid with an excess of magnesium? *Ans.* 196 cc.

120. If 9.8 g. of phosphoric acid is present in 1 liter of a solution, what is (1) the normal concentration and (2) the molar concentration?

121. If 22 g. of strontium hydroxide is present in 6.5 liters of a solution, what is (1) the normal concentration and (2) the molar concentration?
*Ans.* (1) 0.0556 *N*.

122. How many equivalents of a base can be neutralized by 22 cc. of *N*/5 acid? How many grams of base were present if the base was (1) sodium hydroxide, (2) calcium hydroxide? *Ans.* 0.0044 equiv.
0.176 g. NaOH.
0.1628 g. $Ca(OH)_2$.

123. If 10 cc. of a certain sulfuric acid solution yields 0.1220 g. of barium sulfate, how much must the solution be diluted for an exactly *N*/10 solution?
*Ans.* 10 cc. to 10.45 cc.

124. 1.831 g. of zinc was dissolved in an excess of hydrochloric acid, the hydrogen collected over water, and the volume found to be 715 cc. at a temperature of 23° and a pressure of 758 mm. Find the volume of hydrogen, at S.T.P., and the equivalent weight and valence of zinc.
*Ans.* 639.6 cc. hydrogen.
32.11, the equiv. wt.

125. 50 cc. of dilute hydrochloric was required to decompose 2.3 g. of baking soda, and the volume of gas formed occupied 500 cc. at S.T.P. Find the normality of the acid and the percentage of sodium bicarbonate in the baking soda. *Ans.* 0.446 *N*.
81.5 per cent $NaHCO_3$.

126. 18.50 cc. of a decinormal solution of iodine was required in the titration of 25 cc. of a solution of sodium arsenite ($Na_3AsO_3$). What was the normality of the arsenite solution? How many grams of arsenic were present in the sample?

127. Ten cc. of a liquid brass polish containing oxalic acid ($H_2C_2O_4$) required 22.5 cc. of normal sodium hydroxide solution to neutralize it. What weight of oxalic acid did the sample contain?

128. Calculate the equivalent weights of the following oxidizing or reducing agents: potassium dichromate, potassium permanganate in alkaline solution, iodine, Mohr's salt ($FeSO_4 . (NH_4)_2SO_4 . 6H_2O$).

129. 0.2815 g. of calcium carbonate was dissolved in 30 cc. of normal hydrochloric acid and the excess of acid determined by normal sodium hydroxide, of which 24.43 cc. were required. What percentage of carbon dioxide did the sample contain? *Ans.* 43.52 per cent.

130. 0.25 g. of impure pyrolusite was treated with hydrochloric acid and the chlorine passed into an excess of potassium iodide solution. The liberated iodine required for decolorization 50 cc. of a solution of arsenious acid that had been made equivalent to $N/10$ iodine solution. What per cent of manganese dioxide did the pyrolusite contain? *Ans.* 86.9 per cent.

131. A slight excess of barium chloride solution was added to 240 cc. of dilute sulfuric acid, and the barium sulfate precipitated weighed 3.85 g. Calculate the normality of the acid. *Ans.* 0.1375 $N$.

132. 1.156 g. of a solution containing caustic potash was diluted with water and titrated with $N/10$ $H_2SO_4$, of which 36.4 cc. were required. Calculate the percentage of KOH in the sample taken for analysis.
*Ans.* 17.64 per cent.

133. An excess of potassium bicarbonate was added to 125 cc. of dilute sulfuric acid and the volume of gas liberated, measured dry at 20° and 765 mm., was 2.5 liters. Find the normality of the acid.

134. What weight of Mohr's salt would be required to reduce 60 cc. of $N/10$ potassium permanganate?

135. 12.5 cc. of $N/5$ hydrochloric acid would decompose what weight of limestone containing 90 per cent of calcium carbonate? Find the weight of gas liberated.

136. What volume of nitric oxide, measured over water at 21° and 758 mm., could be obtained by the action of 25 cc. of 7 $N$ nitric acid upon pure copper?

137. 0.521 g. of Mohr's salt is dissolved in pure water, acidified with sulfuric acid, and then oxidized by $N/10$ potassium permanganate. What volume of the solution is required, and what weight of permanganate does it contain?

138. A mixture of 2.1 g. of sodium bicarbonate and silica was treated with 50 cc. of dilute hydrochloric acid and the gas formed had a volume of 400 cc. (S.T.P.). Find the percentage of sodium bicarbonate in the mixture and the normality of the acid.

139. How many grams of arsenious oxide are required to prepare a liter of normal arsenious acid for (1) oxidation-reduction reactions, and (2) for neutralization reactions?

140. 10.09 g. of magnesium nitride is heated with excess water, the ammonia evolved is dissolved in water, and the solution diluted to 500 cc. Find the normality of the solution, and the volume of $N/10$ sulfuric acid required to neutralize 10 cc. of this solution.

141. Determine the normality of a potassium dichromate solution, 25 cc. of which oxidized, in acid solution, 1 g. of ferrous sulfate ($FeSO_4 . 7H_2O$) to ferric salt.

142. One gram of a mixture of pure potassium chloride and pure sodium chloride was dissolved in about 100 cc. of water, a few drops of neutral potassium chromate were added, and the chlorine was determined by titration with an exactly $N/10$ solution (neutral) of silver nitrate. 141 cc. were necessary to give the faint red tint. Find the amount of chlorine present, and then calculate the amounts of potassium chloride and sodium chloride in the mixture.

143. Determine the purity of a sample of pyrolusite, 2.2 g. of which, with excess of hydrochloric acid, liberated sufficient chlorine to set free a quantity of iodine that required 250 cc. of $N/5$ sodium thiosulfate for titration.

$$(2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6)$$

144. (*a*) What volume of carbon dioxide, measured dry at 20° and 750 mm., should be absorbed by a solution containing 4 g. of sodium hydroxide, assuming that sodium carbonate is formed?

(*b*) What volume of $N/5$ acetic acid would be required to decompose the salt?

145. If the percentage by volume of carbon dioxide in the air is 0.05, what volume of 0.01 $N$ sodium hydroxide will be required to combine with the

carbon dioxide in a volume of air which occupies one liter at 20° C. and 740 mm.? *Ans.* 4.05 cc.

## SOLUBILITY PRODUCT (221–222)

146. A saturated solution of calcium sulfate is 0.015 molar at 18°. What is its solubility product, assuming complete ionization?

147. If 100 g. of water at 18° dissolves 0.00023 g. of barium sulfate, what is the molar solubility of the salt? Assuming that the solute in the saturated solution is completely ionized, calculate its solubility product.

148. The molar solubility of calcium hydroxide at 18° is 0.02. Assuming that the base in a saturated solution is 90 per cent ionized, calculate its solubility product.

149. The solubility of lead sulfate is 0.00013 mole per liter (18°). Assuming complete ionization of the salt, calculate its solubility product.

150. A liter of a solution of lead hydroxide (18°) contains 0.100 g. of the base. Calculate its solubility product, assuming complete ionization.

# APPENDIX

# APPENDIX

## I. LOGARITHMS

| No. | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | 0000 | 0043 | 0086 | 0128 | 0170 | 0212 | 0253 | 0294 | 0334 | 0374 | 4 | 8 | 12 | 17 | 21 | 25 | 29 | 33 | 37 |
| 11 | 0414 | 0453 | 0492 | 0531 | 0569 | 0607 | 0645 | 0682 | 0719 | 0755 | 4 | 8 | 11 | 15 | 19 | 23 | 26 | 30 | 34 |
| 12 | 0792 | 0828 | 0864 | 0899 | 0934 | 0969 | 1004 | 1038 | 1072 | 1106 | 3 | 7 | 10 | 14 | 17 | 21 | 24 | 28 | 31 |
| 13 | 1139 | 1173 | 1206 | 1239 | 1271 | 1303 | 1335 | 1367 | 1399 | 1430 | 3 | 6 | 10 | 13 | 16 | 19 | 23 | 26 | 29 |
| 14 | 1461 | 1492 | 1523 | 1553 | 1584 | 1614 | 1644 | 1673 | 1703 | 1732 | 3 | 6 | 9 | 12 | 15 | 18 | 21 | 24 | 27 |
| 15 | 1761 | 1790 | 1818 | 1847 | 1875 | 1903 | 1931 | 1959 | 1987 | 2014 | 3 | 6 | 8 | 11 | 14 | 17 | 20 | 22 | 25 |
| 16 | 2041 | 2068 | 2095 | 2122 | 2148 | 2175 | 2201 | 2227 | 2253 | 2279 | 3 | 5 | 8 | 11 | 13 | 16 | 18 | 21 | 24 |
| 17 | 2304 | 2330 | 2355 | 2380 | 2405 | 2430 | 2455 | 2480 | 2504 | 2529 | 2 | 5 | 7 | 10 | 12 | 15 | 17 | 20 | 22 |
| 18 | 2553 | 2577 | 2601 | 2625 | 2648 | 2672 | 2695 | 2718 | 2742 | 2765 | 2 | 5 | 7 | 9 | 12 | 14 | 16 | 19 | 21 |
| 19 | 2788 | 2810 | 2833 | 2856 | 2878 | 2900 | 2923 | 2945 | 2967 | 2989 | 2 | 4 | 7 | 9 | 11 | 13 | 16 | 18 | 20 |
| 20 | 3010 | 3032 | 3054 | 3075 | 3096 | 3118 | 3139 | 3160 | 3181 | 3201 | 2 | 4 | 6 | 8 | 11 | 13 | 15 | 17 | 19 |
| 21 | 3222 | 3243 | 3263 | 3284 | 3304 | 3324 | 3345 | 3365 | 3385 | 3404 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 |
| 22 | 3424 | 3444 | 3464 | 3483 | 3502 | 3522 | 3541 | 3560 | 3579 | 3598 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 15 | 17 |
| 23 | 3617 | 3636 | 3655 | 3674 | 3692 | 3711 | 3729 | 3747 | 3766 | 3784 | 2 | 4 | 6 | 7 | 9 | 11 | 13 | 15 | 17 |
| 24 | 3802 | 3820 | 3838 | 3856 | 3874 | 3892 | 3909 | 3927 | 3945 | 3962 | 2 | 4 | 5 | 7 | 9 | 11 | 12 | 14 | 16 |
| 25 | 3979 | 3997 | 4014 | 4031 | 4048 | 4065 | 4082 | 4099 | 4116 | 4133 | 2 | 3 | 5 | 7 | 9 | 10 | 12 | 14 | 15 |
| 26 | 4150 | 4166 | 4183 | 4200 | 4216 | 4232 | 4249 | 4265 | 4281 | 4298 | 2 | 3 | 5 | 7 | 8 | 10 | 11 | 13 | 15 |
| 27 | 4314 | 4330 | 4346 | 4362 | 4378 | 4393 | 4409 | 4425 | 4440 | 4456 | 2 | 3 | 5 | 6 | 8 | 9 | 11 | 13 | 14 |
| 28 | 4472 | 4487 | 4502 | 4518 | 4533 | 4548 | 4564 | 4579 | 4594 | 4609 | 2 | 3 | 5 | 6 | 8 | 9 | 11 | 12 | 14 |
| 29 | 4624 | 4639 | 4654 | 4669 | 4683 | 4698 | 4713 | 4728 | 4742 | 4757 | 1 | 3 | 4 | 6 | 7 | 9 | 10 | 12 | 13 |
| 30 | 4771 | 4786 | 4800 | 4814 | 4829 | 4843 | 4857 | 4871 | 4886 | 4900 | 1 | 3 | 4 | 6 | 7 | 9 | 10 | 11 | 13 |
| 31 | 4914 | 4928 | 4942 | 4955 | 4969 | 4983 | 4997 | 5011 | 5024 | 5038 | 1 | 3 | 4 | 6 | 7 | 8 | 10 | 11 | 12 |
| 32 | 5051 | 5065 | 5079 | 5092 | 5105 | 5119 | 5132 | 5145 | 5159 | 5172 | 1 | 3 | 4 | 5 | 7 | 8 | 9 | 11 | 12 |
| 33 | 5185 | 5198 | 5211 | 5224 | 5237 | 5250 | 5263 | 5276 | 5289 | 5302 | 1 | 3 | 4 | 5 | 6 | 8 | 9 | 10 | 12 |
| 34 | 5315 | 5328 | 5340 | 5353 | 5366 | 5378 | 5391 | 5403 | 5416 | 5428 | 1 | 3 | 4 | 5 | 6 | 8 | 9 | 10 | 11 |
| 35 | 5441 | 5453 | 5465 | 5478 | 5490 | 5502 | 5514 | 5527 | 5539 | 5551 | 1 | 2 | 4 | 5 | 6 | 7 | 9 | 10 | 11 |
| 36 | 5563 | 5575 | 5587 | 5599 | 5611 | 5623 | 5635 | 5647 | 5658 | 5670 |  | 2 | 4 | 5 | 6 | 7 | 8 | 10 | 11 |
| 37 | 5682 | 5694 | 5705 | 5717 | 5729 | 5740 | 5752 | 5763 | 5775 | 5786 | 1 | 2 | 3 | 5 | 6 | 7 | 8 | 9 | 10 |
| 38 | 5798 | 5809 | 5821 | 5832 | 5843 | 5855 | 5866 | 5877 | 5888 | 5899 | 1 | 2 | 3 | 5 | 6 | 7 | 8 | 9 | 10 |
| 39 | 5911 | 5922 | 5933 | 5944 | 5955 | 5966 | 5977 | 5988 | 5999 | 6010 | 1 | 2 | 3 | 4 | 5 | 7 | 8 | 9 | 10 |
| 40 | 6021 | 6031 | 6042 | 6053 | 6064 | 6075 | 6085 | 6096 | 6107 | 6117 |  | 2 | 3 | 4 | 5 | 6 | 8 | 9 | 10 |
| 41 | 6128 | 6138 | 6149 | 6160 | 6170 | 6180 | 6191 | 6201 | 6212 | 6222 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 42 | 6232 | 6243 | 6253 | 6263 | 6274 | 6284 | 6294 | 6304 | 6314 | 6325 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 43 | 6335 | 6345 | 6355 | 6365 | 6375 | 6386 | 6395 | 6405 | 6415 | 6425 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 44 | 6435 | 6444 | 6454 | 6464 | 6474 | 6484 | 6493 | 6503 | 6513 | 6522 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 45 | 6532 | 6542 | 6551 | 6561 | 6571 | 6580 | 6590 | 6599 | 6609 | 6618 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 46 | 6628 | 6637 | 6646 | 6656 | 6665 | 6675 | 6684 | 6693 | 6702 | 6712 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 7 | 8 |
| 47 | 6721 | 6730 | 6739 | 6749 | 6758 | 6767 | 6776 | 6785 | 6794 | 6803 | 1 | 2 | 3 | 4 | 5 | 5 | 6 | 7 | 8 |
| 48 | 6812 | 6821 | 6830 | 6839 | 6848 | 6857 | 6866 | 6875 | 6884 | 6893 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 | 8 |
| 49 | 6902 | 6911 | 6920 | 6928 | 6937 | 6946 | 6955 | 6964 | 6972 | 6981 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 | 8 |
| 50 | 6990 | 6998 | 7007 | 7016 | 7024 | 7033 | 7042 | 7050 | 7059 | 7067 |  | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 |
| 51 | 7076 | 7084 | 7093 | 7101 | 7110 | 7118 | 7126 | 7135 | 7143 | 7152 | 1 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 |
| 52 | 7160 | 7168 | 7177 | 7185 | 7193 | 7202 | 7210 | 7218 | 7226 | 7235 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 7 | 7 |
| 53 | 7243 | 7251 | 7259 | 7267 | 7275 | 7284 | 7292 | 7300 | 7308 | 7316 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| 54 | 7324 | 7332 | 7340 | 7348 | 7356 | 7364 | 7372 | 7380 | 7388 | 7396 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
|  | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |

LOGARITHMS—*Continued*

| No. | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 55 | 7404 | 7412 | 7419 | 7427 | 7435 | 7443 | 7451 | 7459 | 7466 | 7474 | 1 | 2 | 2 | 3 | 4 | 5 | 5 | 6 | 7 |
| 56 | 7482 | 7490 | 7497 | 7505 | 7513 | 7520 | 7528 | 7536 | 7543 | 7551 | 1 | 2 | 2 | 3 | 4 | 5 | 5 | 6 | 7 |
| 57 | 7559 | 7566 | 7574 | 7582 | 7589 | 7597 | 7604 | 7612 | 7619 | 7627 | 1 | 2 | 2 | 3 | 4 | 5 | 5 | 6 | 7 |
| 58 | 7634 | 7642 | 7649 | 7657 | 7664 | 7672 | 7679 | 7686 | 7694 | 7701 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 |
| 59 | 7709 | 7716 | 7723 | 7731 | 7738 | 7745 | 7752 | 7760 | 7767 | 7774 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 |
| 60 | 7782 | 7789 | 7796 | 7803 | 7810 | 7818 | 7825 | 7832 | 7839 | 7846 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |
| 61 | 7853 | 7860 | 7868 | 7875 | 7882 | 7889 | 7896 | 7903 | 7910 | 7917 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |
| 62 | 7924 | 7931 | 7938 | 7945 | 7952 | 7959 | 7966 | 7973 | 7980 | 7987 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 6 | 6 |
| 63 | 7992 | 8000 | 8007 | 8014 | 8021 | 8028 | 8035 | 8041 | 8048 | 8055 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| 64 | 8062 | 8069 | 8075 | 8082 | 8089 | 8096 | 8102 | 8109 | 8116 | 8122 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| 65 | 8129 | 8136 | 8142 | 8149 | 8156 | 8162 | 8169 | 8176 | 8182 | 8189 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| 66 | 8195 | 8202 | 8209 | 8215 | 8222 | 8228 | 8235 | 8241 | 8248 | 8254 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| 67 | 8261 | 8267 | 8274 | 8280 | 8287 | 8293 | 8299 | 8306 | 8312 | 8319 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| 68 | 8325 | 8331 | 8338 | 8344 | 8351 | 8357 | 8363 | 8370 | 8376 | 8382 | 1 | 1 | 2 | 3 | 3 | 4 | 4 | 5 | 6 |
| 69 | 8388 | 8395 | 8401 | 8407 | 8414 | 8420 | 8426 | 8432 | 8439 | 8445 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 6 |
| 70 | 8451 | 8457 | 8463 | 8470 | 8476 | 8482 | 8488 | 8494 | 8500 | 8506 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 6 |
| 71 | 8513 | 8519 | 8525 | 8531 | 8537 | 8543 | 8549 | 8555 | 8561 | 8567 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 72 | 8573 | 8579 | 8585 | 8591 | 8597 | 8603 | 8609 | 8615 | 8621 | 8627 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 73 | 8633 | 8639 | 8645 | 8651 | 8657 | 8663 | 8669 | 8675 | 8681 | 8686 | 1 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 5 |
| 74 | 8692 | 8698 | 8704 | 8710 | 8716 | 8722 | 8727 | 8733 | 8739 | 8745 | 1 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 5 |
| 75 | 8751 | 8756 | 8762 | 8768 | 8774 | 8779 | 8785 | 8791 | 8797 | 8802 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 5 |
| 76 | 8808 | 8814 | 8820 | 8825 | 8831 | 8837 | 8842 | 8848 | 8854 | 8859 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 5 |
| 77 | 8865 | 8871 | 8876 | 8882 | 8887 | 8893 | 8899 | 8904 | 8910 | 8915 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 78 | 8921 | 8927 | 8932 | 8938 | 8943 | 8949 | 8954 | 8960 | 8965 | 8971 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 79 | 8976 | 8982 | 8987 | 8993 | 8998 | 9004 | 9009 | 9015 | 9020 | 9025 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 80 | 9031 | 9036 | 9042 | 9047 | 9053 | 9058 | 9063 | 9069 | 9074 | 9079 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 81 | 9085 | 9090 | 9096 | 9101 | 9106 | 9112 | 9117 | 9122 | 9128 | 9133 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 82 | 9138 | 9143 | 9149 | 9154 | 9159 | 9165 | 9170 | 9175 | 9180 | 9186 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 83 | 9191 | 9196 | 9201 | 9206 | 9212 | 9217 | 9222 | 9227 | 9232 | 9238 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 84 | 9243 | 9248 | 9253 | 9258 | 9263 | 9269 | 9274 | 9279 | 9284 | 9289 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 85 | 9294 | 9299 | 9304 | 9309 | 9315 | 9320 | 9325 | 9330 | 9335 | 9340 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 86 | 9345 | 9350 | 9355 | 9360 | 9365 | 9370 | 9375 | 9380 | 9385 | 9390 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 87 | 9395 | 9400 | 9405 | 9410 | 9415 | 9420 | 9425 | 9430 | 9435 | 9440 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 88 | 9445 | 9450 | 9455 | 9460 | 9465 | 9469 | 9474 | 9479 | 9484 | 9489 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 89 | 9494 | 9499 | 9504 | 9509 | 9513 | 9518 | 9523 | 9528 | 9533 | 9538 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 90 | 9542 | 9547 | 9552 | 9557 | 9562 | 9566 | 9571 | 9576 | 9581 | 9586 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 91 | 9590 | 9595 | 9600 | 9605 | 9609 | 9614 | 9619 | 9624 | 9628 | 9633 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 92 | 9638 | 9643 | 9647 | 9652 | 9657 | 9661 | 9666 | 9671 | 9675 | 9680 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 93 | 9685 | 9689 | 9694 | 9699 | 9703 | 9708 | 9713 | 9717 | 9722 | 9727 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 94 | 9731 | 9736 | 9741 | 9745 | 9750 | 9754 | 9759 | 9763 | 9768 | 9773 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 95 | 9777 | 9782 | 9786 | 9791 | 9795 | 9800 | 9805 | 9809 | 9814 | 9818 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 96 | 9823 | 9827 | 9832 | 9836 | 9841 | 9845 | 9850 | 9854 | 9859 | 9863 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 97 | 9868 | 9872 | 9877 | 9881 | 9886 | 9890 | 9894 | 9899 | 9903 | 9908 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 98 | 9912 | 9917 | 9921 | 9926 | 9930 | 9934 | 9939 | 9943 | 9948 | 9952 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 99 | 9956 | 9961 | 9965 | 9969 | 9974 | 9978 | 9983 | 9987 | 9991 | 9996 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 3 | 4 |
|  | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |

## II. Weights and Measures

### METRIC SYSTEM

*Measures of Length*

| *Meter* | | *Decimeters* | | *Centimeters* | | *Millimeters* | | *Inches* |
|---|---|---|---|---|---|---|---|---|
| 1 | = | 10 | = | 100 | = | 1000 | = | 39.37100 |

*Measures of Capacity*

| *Liter* | | *Cubic Centimeters* | | *Pints* | | *Cubic inches* |
|---|---|---|---|---|---|---|
| 1 | = | 1000 | = | 2.113 (U.S.) | = | 61.0363 |
| | | 1 | = | 0.002113 (U.S.) | = | 0.0610 |
| | | 16.38 | | | = | 1.00 |

*Measures of Weight*

| *Kilogram* | | *Grams* | | *Lbs.* (*Avoirdupois*) | | *Grains* |
|---|---|---|---|---|---|---|
| 1 | = | 1000 | = | 2.2046 | = | 15432.00 |
| | | 1 | = | 0.0022 | = | 15.43 |

Linear . . . . .
10 millimeters (mm) = 1 centimeter (cm).
10 centimeters = 1 decimeter (dm).
10 decimeters = 1 meter (m).
Equivalent. 1 inch = 2.54 cm (nearly).

Cubic . . . . . .
1000 cubic millimeters = 1 cubic centimeter (cc).
1000 cubic centimeters = 1 cubic decimeter (cdm).
1000 cubic decimeters = 1 cubic meter (cbm).
Equivalents 1000 cc = 1 liter (1l).
Equivalents 1l = 1 quart (nearly).

Weight . . . .
10 milligrams (mg) = 1 centigram (cg).
10 centigrams = 1 decigram (dg).
10 decigrams = 1 gram (g).*
1000 grams = 1 kilogram (kg).

Conversion .
1cc of water (at 4° C.) = 1g.
1l of water (at 4° c.) = 1kg.
28.3g = 1 oz. (nearly).
1kg = 2⅕ lb. (nearly).
1g = 15 gr. (nearly).
1000k = 2205 lbs. = 1 metric ton.
1 lb. avoird. = 453.6 g.

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*To be exact, 1 g. of water at 4° C. and 760 mm. occupies 1.000027 cc. This volume is called a milliliter (ml.). It is used instead of the cubic centimeter in very exact work. The milliliter is 0.0027 per cent larger than the cubic centimeter.

## III. Vapor Pressures of Water Expressed in Millimeters of Mercury

| | |
|---|---|
| 0° | 4.6 |
| 5° | 6.5 |
| 10° | 9.1 |
| 11° | 9.8 |
| 12° | 10.4 |
| 13° | 11.1 |
| 14° | 11.9 |
| 15° | 12.7 |
| 16° | 13.5 |
| 17° | 14.4 |
| 18° | 15.3 |
| 19° | 16.3 |
| 20° | 17.4 |
| 21° | 18.5 |
| 22° | 19.6 |
| 23° | 20.9 |
| 24° | 22.2 |
| 25° | 23.7 |
| 26° | 25.0 |
| 27° | 26.5 |
| 28° | 28.1 |
| 29° | 29.7 |
| 30° | 31.5 |
| 40° | 54.9 |
| 50° | 92.0 |
| 60° | 148.9 |
| 70° | 233.3 |
| 80° | 354.9 |
| 90° | 525.5 |
| 97° | 681.9 |
| 100° | 760.0 |
| 120° | 1491.3 |
| 150° | 3581.2 |
| 180° | 7546.4 |
| 220° | 17390.4 |

## IV. Corrections for Reading of the Barometer from 15° C. to 30° C., and at 750 mm.

The column of mercury expands with rising temperature, consequently a correction must be made in order to reduce the column of mercury to 0° C.

| *Temperature* | *Correction for Barometer with Glass Scale* | *Correction for Barometer with Brass Scale* |
|---|---|---|
| 15° | 2. mm. | 1.8 mm. |
| 16 | 2.1 | 2.0 |
| 17 | 2.2 | 2.1 |
| 18 | 2.3 | 2.2 |
| 19 | 2.5 | 2.3 |
| 20 | 2.6 | 2.5 |
| 21 | 2.7 | 2.6 |
| 22 | 2.8 | 2.7 |
| 23 | 3.0 | 2.8 |
| 24 | 3.1 | 2.9 |
| 25 | 3.2 | 3.1 |
| 26 | 3.4 | 3.2 |
| 27 | 3.5 | 3.3 |
| 28 | 3.6 | 3.4 |
| 29 | 3.7 | 3.6 |
| 30 | 3.9 | 3.7 |

## V. Scale of Hardness

1. Talc
2. Rock Salt (or Gypsum)
3. Calcite
4. Fluorite
5. Apatite
6. Orthoclase (Potash Feldspar)
7. Quartz
8. Topaz
9. Corundum
10. Diamond

Each mineral in this list will scratch the surface of any one preceding it.

## VI. Some Physical Properties of Some of the Metals

| *Metal* | *Density (Mass of 1 cc.)* | *Melting Point °C.* | *Boiling Point °C.* |
|---|---|---|---|
| Aluminium | 2.7 | 658.7 | 1800 |
| *Antimony | 6.68 | 630 | 1635 |
| *Arsenic | 5.73 | 814(36 atm.) | 615 |
| Barium | 3.5 | 850 | 1140 |
| Beryllium | 1.85 | 1350 | 1530 |
| *Bismuth | 9.78 | 271 | 1450 |
| Cadmium | 8.65 | 321 | 778 |
| Calcium | 1.55 | 810 | 1439 |
| Cerium | 6.9 | 640 | 1400 |
| Chromium | 7.1 | 1615 | 2200 |
| Cobalt | 8.9 | 1480 | 2900 |
| Copper | 8.94 | 1083 | 2310 |
| Gold | 19.3 | 1063 | 2600 |
| Iridium | 22.4 | 2440 | 4400 |
| Iron | 7.86 | 1535 | 3000 |
| Lead | 11.35 | 327.5 | 1620 |
| Lithium | 0.53 | 186 | 1336 |
| Magnesium | 1.74 | 651 | 1110 |
| Manganese | 7.2 | 1260 | 1900 |
| Mercury | 13.595 (4°) | −38.89 | 357 |
| Molybdenum | 10.2 | 2620 | 3700 |
| Nickel | 8.9 | 1452 | 2900 |
| Osmium | 22.48 | 2700 | 4450 |
| Palladium | 11.4 | 1555 | 2200 |
| Platinum | 21.45 | 1755 | 4050 |
| Potassium | 0.86 | 62.3 | 760 |
| Silver | 10.5 | 960.5 | 1950 |
| Sodium | 0.97 | 97.5 | 880 |
| Strontium | 2.6 | 752 | 1150 |
| Tantalum | 16.6 | 2850 | >4100 |
| Thallium | 11.85 | 303.5 | 1650 |
| Tin | 7.31 | 231.9 | 2270 |
| Titanium | 4.5 | 1800 | >3000 |
| Tungsten | 19.3 | 3370 | 4727 |
| Vanadium | 5.87 | 1715 | 3400 |
| Zinc | 7.14 | 419.4 | 907 |

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* Also classed as non-metals.

## VII. SOME PHYSICAL PROPERTIES OF SOME OF THE NON-METALS

| *Non-metal* | *Density (Mass of 1 cc.)* | *Melting Point °C.* | *Boiling Point °C.* |
|---|---|---|---|
| Boron | 2.3 | >2000 | 2550 sublimes |
| Bromine | 3.12 liq. | −7.2 | 58.5 |
| Carbon | amor. 1.88<br>graphite 2.25<br>diamond 3.5 | 3500 sublimes | 4200 |
| Chlorine | 1.87 | −101.6 | −34.6 |
| Fluorine | 1.11@−187° | −223 | −187 |
| Iodine | 4.93 | 113.5 | 183 |
| Nitrogen | 0.808<br>@−195.8 | −209.9 | −195.8 |
| Oxygen | 1.14<br>@−183 | −218.7 | −183.0 |
| Phosphorus | yellow: 1.82<br>red: 2.20 | 44.1 | 280 |
| Selenium | 4.3−8 | 217 | 688 |
| Silicon | 2.4 | 1420 | 2600 |
| Sulfur | rhombic: 2.07 | 112.8 | 446 |
|  | monoclinic: 1.96 | 119 | 446 |

## VIII. SOME SOLUBILITY PRODUCTS

| | |
|---|---|
| Halides | |
| AgBr | $4\times10^{-13}$ |
| AgCl | $1\times10^{-10}$ |
| AgI | $1\times10^{-16}$ |
| $CaF_2$ | $3.5\times10^{-11}$ |
| HgCl | $3\times10^{-18}$ |
| Carbonates | |
| $BaCO_3$ | $7\times10^{-9}$ |
| $CaCO_3$ | $1\times10^{-8}$ |
| $MgCO_3$ | $2\times10^{-4}$ |
| $PbCO_3$ | $3\times10^{-14}$ |
| $SrCO_3$ | $1.6\times10^{-9}$ |
| Hydroxides | |
| $Al(OH)_3$ | $3.7\times10^{-15}$ |
| $Fe(OH)_2$ | $3\times10^{-14}$ |
| $Fe(OH)_3$ | $1\times10^{-36}$ |
| $Mg(OH)_2$ | $1\times10^{-11}$ |
| $Zn(OH)_2$ | $2\times10^{-23}$ |

| | |
|---|---|
| Sulfides | |
| $Ag_2S$ | $1.6\times10^{-49}$ |
| CdS | $4\times10^{-29}$ |
| CuS | $2\times10^{-47}$ |
| FeS | $3.7\times10^{-19}$ |
| HgS | $4\times10^{-53}$ |
| MnS | $1.4\times10^{-15}$ |
| NiS | $1.4\times10^{-24}$ |
| PbS | $1\times10^{-29}$ |
| ZnS | $1\times10^{-23}$ |
| Sulfates | |
| $BaSO_4$ | $1\times10^{-10}$ |
| $PbSO_4$ | $1\times10^{-8}$ |
| $SrSO_4$ | $3\times10^{-7}$ |
| Chromates | |
| $Ag_2CrO_4$ | $2\times10^{-12}$ |
| $BaCrO_4$ | $2\times10^{-10}$ |
| $PbCrO_4$ | $2\times10^{-14}$ |

## IX. ATOMIC RADII OF ELEMENTS

(In Ångstrom Units)

One Ångstrom Unit = $10^{-8}$ centimeter = $10^{-7}$ millimeter.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Li | 1.50 | Be | 1.14 | Al | 1.43 | Ni | 1.24 | Sn | 1.51 |
| Na | 1.86 | Mg | 1.60 | Cr | 1.25 | Cu | 1.28 | Pb | 1.75 |
| K | 2.27 | Ca | 1.97 | Mn | 1.28 | Zn | 1.32 | Ag | 1.44 |
| Rb | 2.44 | Sr | 2.14 | Fe | 1.24 | Cd | 1.49 | Au | 1.44 |
| Cs | 2.62 | Ba | 2.17 | Co | 1.26 | Hg | 1.50 | Pt | 1.38 |

## X. RADII OF IONS

(In Ångstrom Units)

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $H^-$ | 1.27 | $F^-$ | 1.33 | $Cl^-$ | 1.81 | $Br^-$ | 1.96 | $I^-$ | 2.19 | | |
| $Li^+$ | 0.68 | $Na^+$ | 0.98 | $K^+$ | 1.33 | $Rb^+$ | 1.48 | $Cs^+$ | 1.67 | $Ag^+$ | 1.13 |
| $Be^{2+}$ | 0.39 | $Mg^{2+}$ | 0.71 | $Ca^{2+}$ | 0.98 | $Sr^{2+}$ | 1.15 | $Ba^{2+}$ | 1.31 | | |
| $Mn^{2+}$ | 0.91 | $Fe^{2+}$ | 0.83 | $Co^{2+}$ | 0.82 | $Ni^{2+}$ | 0.78 | $Zn^{2+}$ | 0.83 | | |
| $Al^{3+}$ | 0.55 | $Cr^{3+}$ | 0.65 | $Mn^{3+}$ | 0.70 | $Fe^{3+}$ | 0.67 | $Pt^{4+}$ | 0.55 | | |

## XI. SOLUBILITIES OF SOME SALTS AT 20° C.

Expressed as the number of grams of the anhydrous salt held in solution by 100 cc. of water. In a few cases the temperature is other than 20°: in these instances the temperature is noted as a superscript. Notation: $0.0_62$ means 0.0000002.

| | $Ag^+$ | $Al^{+++}$ | $Ba^{++}$ | $Ca^{++}$ | $K^+$ | $Li^+$ | $Mg^{++}$ | $Na^+$ | $Pb^{++}$ | $Sn^{++}$ | $Sr^{++}$ | $Zn^{++}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Br^-$ | $0.0_584$ | — | 104 | 144 | 65.2 | 177 | 96.5 | 90 | 0.85 | $85.2^0$ | 102.4 | 477 |
| $BrO_3^-$ | 0.8 | — | 0.65 | 8.6 | 6.9 | 155 | 27 | 34.5 | 1.32 | — | 31 | 70 |
| $Cl^-$ | $0.0_315$ | 43 | 35.7 | 74.5 | 34.0 | 78.5 | 54.5 | 36.0 | 0.99 | 270 | 52 | $432^{25}$ |
| $ClO_3^-$ | 12.3 | — | 25.26 | 179.3 | 7.4 | 313.4 | 33 | 101 | $151^{18}$ | — | $174.9^{18}$ | 200 |
| $CO_3^{=}$ | 0.0032 | — | 0.0022 | 0.0013 | 112 | 1.33 | 0.1 | 21.5 | $0.0_311$ | — | 0.0015 | 0.001 |
| $C_2O_4^{=}$ | $0.0_335$ | — | 0.01 | $0.0_36$ | 33 | 7.22 | 0.055 | 3.7. | $0.0_316$ | — | 0.0046 | $0.0_38$ |
| $CrO_4^{=}$ | 0.003 | — | $.0_337$ | 20 | 61.7 | 111.6 | 110 | 65 | $0.0_57$ | — | $0.12^{15}$ | — |
| $F^-$ | 196 | — | 0.16 | 0.0017 | 94 | 0.3 | 0.008 | 4.44 | 0.064 | — | 0.012 | $0.005^{18}$ |
| $I^-$ | $0.0_63$ | — | 205 | 68 | 144 | 165 | $100^0$ | 178.7 | 0.068 | 1.0 | 177.8 | $430^0$ |
| $IO_3^-$ | 0.004 | — | 0.002 | 0.1 | 8.13 | $125^{15}$ | 86 | 9 | 0.003 | — | $0.25^{18}$ | $0.8^{18}$ |
| $NO_2^-$ | 0.34 | — | 40.3 | $37^0$ | 309 | $125^0$ | — | — | — | — | — | — |
| $NO_3^-$ | 222 | 36.2 | 9.2 | 330 | 31.6 | $71.4^{18}$ | $35^{18}$ | 88 | 56.5 | — | 86 | 110 |
| $OH^-$ | 0.01 | — | 3.89 | 0.165 | 112 | 12.08 | 0.001 | 109 | 0.0155 | — | 0 8 | $0.0_63$ |
| $SO_3^{=}$ | — | — | 0.02 | 0.03 | 84 | — | 0.5 | 26.9 | — | — | — | 0.13 |
| $SO_4^{=}$ | 0.79 | 26.7 | $.0_324$ | 0.20 | 11.11 | 25 | $26^0$ | 50 | 0.0041 | 19 | 0.0114 | $53^{18}$ |

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29. **Liquid air.** CADY. 8, 1027–1043 (1931). Striking photographs and descriptions. *Caution:* do not burn Al in liquid oxygen.

30. **The story of nickel.** BALDWIN. 8, 1749–61; 1954–68; 2325–40 (1931). History of the industry; industrial importance; detailed metallurgy. An excellent treatment; many pictures.

### REFERENCES FROM THE JOURNAL OF CHEMICAL EDUCATION (CONTINUED)

31. **The borax industry in Southern California.** DINGLEY. 8, 2112–2125 (1931). Location of deposits; uses; nothing on process of refining. Several pictures.

32. **On ozone.** WORSTELL. 9, 291–300 (1932). A chemical resumé.

33. **Ceramics and chemistry.** KINGSBURY. 9, 794–819 (1932). Photomicrographs; ancient and modern products; glazing details; diverse applications of stoneware in chemical industry.

34. **Recent developments in the rubber industry.** OENSLAGER. 9, 974–99 (1932). Ingredients in an automobile tire; vulcanizing; uses of latex; mechanical handling.

35. **Studies in the mineral and chemical resources of the Mojave Desert.** TURRILL. 9, 1318–39; 1530–52 (1932). Location; by-products of the potash and borax industries; Death Valley area.

36. **Extinguishing fires with chemicals.** SCHEFLAN. 9, 1503–22 (1932). Many photographs of types of extinguishers and their special uses; no chemistry.

37. **Variations in the prices of metals in the last twenty years.** BAILAR. 10, 99–107. (1933). Interesting study; numerous graphs.

38. **Cellulose and its place in industry.** SCHERER. 10, 131–40 (1933). Pure cellulose, chemical properties and uses.

39. **The derivations of the names of the elements.** HAUBEN. 10, 227–34 (1933). History of discovery, as well as etymological. See also 15, 123–6 (1938).

40. **Sources of ores of the ferroalloy metals.** BURCHARD. 10, 359–68 (1933). Supplements papers on iron ore deposits. Description; geology.

41. **Crystal chemistry for college freshmen.** STILLWELL. 10, 590–9; 667–74 (1933); and 11, 159 (1934). By the same author 13, 415; 469; 521; 566 (1936); 14, 35, 131 (1937). Considerably advanced treatment.

42. **Colloids in biochemistry.** GORTNER. 11, 279–83 (1934). An appreciation of Thomas Graham, showing that his interest in colloids grew out of studies on diffusion.

43. **Emeralds.** HOWARD. 11, 323–7 (1934). Excellent bibliography although no chemistry in the article.

44. **Some early thermometers.** BROWN. 11, 448–53 (1934). Sixteen plates of ancient thermometers; no chemistry.

45. **The pronunciation of chemical words.** CRANE. 11, 454 (1934). Also *Ind. Eng. Chem., News Ed.* 12, 202–5 (1934). Rules and pronunciations for 437 words.

46. **A century of progress in the paint industry.** HECKEL. 11, 487–93 (1934). Historical survey of the ingredients of modern paint.

### REFERENCES FROM THE JOURNAL OF CHEMICAL EDUCATION (CONTINUED)

47. **Sulfur.** CUNNINGHAM. 12, 17–23; 83–87; 120–4 (1935). Early sulfur production; modern technical details; excellent review of properties.

48. **The production of salt.** HYLER. 12, 203–7 (1935). Brief account of industrial treatment.

49. **Metals and alloys in the chemical industry.** ROHRMAN. 13, 53–9 (1936). Survey of reaction vessels; several plates.

50. **Titanium and its more useful compounds.** MCKINNEY and MADSON. 13, 155–159 (1935). Chemical review, with commercial developments.

51. **Fritz Haber.** BERL. 14, 203–7 (1937). Excellent obituary.

52. **The production of electrotypes.** RONNENBERG. 14, 303–10 (1937). Many photographs; an interesting chemical presentation. See also 15, 565–75 (1938).

53. **The ferric thiocyanate equilibria.** DUBOIS. 14, 324–6 (1937).

54. **Chemical warfare in the middle ages.** CHERONS. 14, 260 (1937). Kallinikos, "Prepared fire." An interesting historical sketch.

55. **The row of increasing atomic weights and the periodic law.** GROSSE. 14, 433–44 (1937). Interesting tables and graphs, showing stable and unstable isotopes.

56. **Henry LeChatelier: 1850 to 1936.** SILVERMAN. 14, 555–60 (1937). An obituary. See also 15, 289–90 (1938).

57. **The metal carbonyls.** TROUT. 14, 453–9; 575–81 (1937); 15, 77–83; 113–21 (1938). Advanced chemistry.

58. **Lakes as a chemist sees them.** ROBINSON. 1[illegible] 209–13 (1938). Water temperatures; dissolved gases; plants; chemical elements.

59. **Count Michael Maier's use of the symbolism of alchemy.** DAVIS. 15, 403–10 (1938). Eleven plates; ancient quotations; interesting account.

60. **The monkey models of the benzene ring.** 15, 444 (1938). Two pictures with caption—not a reading assignment.

61. **Electrochemistry of rare metals.** FINK. 16, 108–12 (1939). Electric furnace and electrolytic cell developments for metals in all eight groups.

62. **Colloidal graphite.** SZYMANOWITZ. 16, 413–22 (1939). History of colloids; preparation of graphite; X-ray studies; uses. Good survey.

63. **New products of the rubber industry.** REYNOLDS. 16, 486–91. (1939).

64. **A rule of coordination valency.** ROBEY. 16, 514–16 (1939). Advanced.

65. **The atomic hypothesis of William Higgins.** ATKINSON. 17, 3–11 (1940). Historical sketch of a scientist who claimed to have anticipated Dalten's atomic theory. Many portraits.

### REFERENCES FROM THE JOURNAL OF CHEMICAL EDUCATION (CONTINUED)

66. **Latin and Greek roots in chemical terminology.** BEEZER. **17,** 63–6 (1940).

67. **Some recent advances in colloids.** MCBAIN. 17, 109–11 (1940). Good but brief.

68. **Acid-base symposium.** HALL. BRISCOE. HAMMETT. JOHNSON. 17, 124–36 (1939). Controversial and advanced.

69. **Fluospar—its chemical and industrial applications.** SCHWERIN. 17, 160–5 (1940). Good; chemical.

70. **Metallurgy of tungsten and molybdenum.** SYKES. 17, 190–2 (1940). Excellent; photomicrographs.

71. **Early Pennsylvania pottery.** BILLINGER. 17, 407–13 (1940). Extensively illustrated.

72. **Extraction of radium from Canadian pitchblende.** KUEBEL. 17, 417–22 (1940). Chemical treatments; eight figures.

73. **Phenolphthalein and methyl orange.** PETERS and REDMON. 17, 525–8 (1940). Structural formulas and discussion of color changes. Knowledge of organic chemistry required.

74. **Isotopes as indicators.** ROSENBLUM. 17, 567–70 (1940). Advanced. Also BREWER: **Isotopes in the study of plant growth. 20,** 217–21 (1940).

75. **Water: Some interpretations more or less recent.** FORBES. 18, 18–24 (1941). Advanced; excellent discussion of structure, hydration, ionic radii, energy.

76. **Some problems of chemotherapy.** BURGER. 18, 58–62 (1941). Historical; formulas of a large number of therapeutics.

77. **A history of the match industry.** CRASS. 18, 116–20; 277–82 (1941). From phosphorous to the safety match.

78. **The coordination theory and coordination compounds of the platinum group metals.** KELLER. 18, 134–42 (1941). Advanced.

79. **The electron microscope.** ALYEA. 18, 236–7 (1941).

80. **Recent advances in the chemistry of the proteins.** CARPENTER. 18, 274–6 (1941). Advanced; structural formulas.

### REFERENCES FROM FORTUNE MAGAZINE

(A reading time is indicated for each article.)

100. **Sand into glass. 1,** 69 (1930), *February.* Composition; manufacture of artistic glassware. ½ *hr.*

101. **Allied Chemical and Dye. 1,** 81 (1930), June. Products; nitrogen fixation and statistics. ½ *hr.*

102. **Properties versus principles. 1,** 84 (1930), *June.* Pure versus applied science: Lavoisier, Langmuir tungsten, Acheson carborundum, Whitaker absolute alcohol, Beckert steel, Moore helium. ½ *hr.*

### REFERENCES FROM FORTUNE MAGAZINE (CONTINUED)

103. **Nitrogen.** 2, 55 (1930), *October.* International agreements; Chile; German production; costs. *1 hr.*

104. **Atom S.** 2, 79 (1930), *October.* Importance of sulfur; U. S. control. ½ *hr.*

105. **Modern stained glass.** 2, 74 (1930), *December.* Modern artists; process of making stained-glass windows; colored illustrations. ½ *hr.*

106. **$2NaCl + 2H_2O \rightarrow 2NaOH + Cl_2 + H_2$.** 3, 58 (1931), *April.* Dow brines and products: halogens; electrolysis of brine; chlorine compounds; Mg alloys. ½ *hr.*

107. **Steel III: Mill on the lake.** 4, 41 (1931), *September.* Inland Steel Co. from ore through the metallurgy of steel. *1 hr.*

108. **Limestone, a portfolio.** 4, 66 (1931), *September.* Seven superb pictures; no reading matter.

109. **Alaska Juneau—gold mine.** 5, 30 (1932), *January.* Geology of deposits; chemistry of milling operations; costs. ½ *hr.*

110. **Just all about cellophane.** 5, 74 (1932), *February.* History of Du Pont enterprise. ½ *hr.*

111. **Sunlight and shadow.** 5, 50 (1932), *May.* Eastman Kodak processes of manufacturing film; costs; customers; research. *1½ hrs.*

112. **Tin.** 5, 74 (1932), *May.* Geography; Bolivia; tin control. *1½ hrs.*

113. **109 degrees below zero.** 6, 74 (1932), *July.* Dry Ice; history of its exploitation; costs; uses. ½ *hr.*

114. **Nitrogen.** 6, 43 (1932), *August.* Historical; Haber; in war and peace; world economics, future costs. More exhaustive a treatment than reference 103. *2½ hrs.*

115. **The marble of Vermont.** 6, 46 (1932), *October.* Cost; comparison with European marbles; excellent pictures. ½ *hr.*

116. **Twenty Mule Team Borax.** 6, 40 (1932), *November.* History and industrial story of competitive companies. ½ *hr.*

117. **Water still freezes.** 7, 73 (1933), *May.* Industrial ice from ammonia refrigerators by American Ice. ½ *hr.*

118. **Gold in Canada.** 7, 30 (1933), *June.* Geology; location; mining by General Airways. *1 hr.*

119. **Air reduction.** 8, 24 (1933), *July.* Oxy-acetylene; alcohol; rare gases. ½ *hr.*

120. **Swiss Family Dreyfus.** 8, 50 (1933), *October.* The history of viscose; financing, Du Pont. *1 hr.*

121. **The great radium mystery.** 9, 70 (1934), *February.* LaBine's discovery; Canadian versus the Congo radium. *1 hr.*

122. **Four walls around an industry.** 10, 64 (1934), *August.* International Nickel; nickel metallurgy; properties of nickel alloys. *1 hr.*

123. **The Aluminum Company of America.** 10, 46 (1934), *Sep-*

REFERENCES FROM FORTUNE MAGAZINE (CONTINUED)

*tember.* History of the company; producer and fabricator; competitive companies. *1 hr.*

124. **Salt of the island.** 10, 78 (1934), *November.* Operations by the International Salt Co.; seven excellent pictures on salt treatment. *10 min.*

125. **Du Pont, Part II. An industrial empire.** 10, 80 (1934), *December.* Nitrocellulose products; viscose; cellophane; tetraethyl lead; lacquers; explosives; dyes; the management. *2 hrs.*

126. **Diamonds.** 11, 66 (1935), *May.* Location of diamonds, history of Kimberley, the diamond syndicate. *1½ hrs.*

127. **Doing something for silver.** 12, 74 (1935), *July.* Operation data on U. S. Smelting, Refining and Mining Company in Mexico, Utah and Alaska. *1 hr.*

128. **Hercules Powder.** 12, 56 (1935), *September.* Cellulose explosives. *1 hr.*

129. **What man has joined together.** 13, 68 (1938), *March.* Celluloid; Bakelite; other plastics. *1 hr.*

130. **Element number forty-two.** 14, 105 (1936), *October.* Molybdenum history; special steels. *1 hr.*

131. **Anaconda.** 14, 82, 19 (1936), *December*; and 15, 70 (1937), *January.* Copper statistics; metallurgy; brass and other alloys. *3 hrs.*

132. **Gas masks.** 14, 120 (1936), *December.* Principle of gas masks (good diagram); psychological effect. *1 hr.*

133. **Chemical Industry.** 16, 82 (1937), *December.* Modern research methods; growth of chemical industries; policies. *1½ hrs.*

134. **The deepest hole in the world.** 18, 50 (1938), *July.* A petroleum oil well three miles deep. *½ hr.*

135. **In the light of Poloroid.** 18, 74 (1938), *September.* Poloroid glass; what it is, and its history. *½ hr.*

136. **Houdry process.** 19, 56 (1939), *February.* Organization; flow-sheet; Houdry's part.

137. **Globe Iron Co.** 19, 53 (1939), *March.* Types of ores; plants; costs.

138. **Hiram Walker Whiskey.** 19, 68 (1939), *March.* Flow-sheet of process; history of management; sales.

139. **Lonely Lenox: An idyl in fine china.** 19, 60 (1939), *April.* The art of china; glaze; little chemistry.

140. **Germany.** 20, 55 (1939), *October.* "Ersatz" (substitute) substances to make her self-sufficient. 20, 43 (1939), *November.* Also 20, 92 (1939), *December.* Resources in Germany and conquered countries.

141. **Crucible steel.** 20, 75 (1939), *November.* Composition and properties of alloys and their uses; management.

### REFERENCES FROM FORTUNE MAGAZINE (CONTINUED)

142. **U. S. Industrialization.** 21, 50 (1940), *February.* Raw materials; numerous charts.

143. **The Incredible Barco.** 21, 76 (1940), *March.* Picture album of adventure in Colombian oil.

144. **Goodrich mechanical rubber.** 21, 65 (1940), *June.* Hard rubber uses; electroplating rubber; rubber foam; Koroseal; butadiene rubber.

145. **Blood, toil, tears and sweat.** 22, 52 (1940), *July.* Superb colored chart of strategic materials produced throughout the world.

146. **Nylon.** 22, 57 (1940), *July.* Excellent flow-sheets of processes; much chemistry.

147. **Natural gas.** 22, 56 (1940), *August.* Maps of pipe lines; companies; geology of gas; laying pipe; relation to coal; government control.

148. **Abbott Laboratories.** 22, 63 (1940), *August.* Drug ethics and profits; some drugs it manufactures.

149. **Synthetic rubber.** 22, 71 (1940), *August.* Ameripol; Neoprene; butyl rubber; economics; raw materials.

150. **American Cyanamid.** 22, 66 (1940), *September.* Fertilizer; management; Calco dyes; Lederle drugs; research.

151. **National defense.** 22, 52 (1940), *October.* Excellent maps showing raw materials and industries.

152. **Plastics in 1940.** 22, 89 (1940), *October.* History of producers; raw materials and finished plastics listed; types of molds; laminations; future.

153. **Union Carbide.** 23, 61 (1941), *June.* Map of products; organization.

### REFERENCES FROM THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY

(A reading time is indicated for each article.)

200. **The Perkin Medal Award to C. M. Hall.** 3, 143–51 (1911). Hall's and Heroult's own accounts. *2½ hrs.*

201. **Perkin Medal Award to H. Frasch.** 4, 132–47 (1912). Account of the research which developed the sulfur process. *4½ hrs.*

202. **Synthesis of precious stones.** LEVIN. 5, 495–500 (1913). Diamonds; emeralds; rubies; sapphires. *1½ hrs.*

203. **Willard Gibbs Medal Award to W. R. Whitney.** 8, 559–64 (1916). Applied research in the field of carbon arcs, high vacuum, tungsten filament lamps, argon lamps. *2 hrs.*

204. **New alloys to replace platinum.** FAHRENWALD. 9, 590–7 (1917). *1 hr.*

205. **The American spirit in chemistry.** E. F. SMITH. 11, 405–10 (1919). Young followers of Joseph Priestley. *1 hr.*

### REFERENCES FROM THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY (CONTINUED)

206. **The American potash industry and its problems.** TEEPLE. **13,** 249–52 (1921). The chemistry of treating the Searles Lake deposits of potash and borax; technical. *½ hr.*

207. **Ernest Solvay—an appreciation.** NICHOLS. **14,** 1156–8 (1922). Conception and development of Solvay process; historical; little chemistry. *½ hr.*

208. **Robert Brown and the discovery of the Brownian movement.** NEWELL. **15,** 1279 (1923). Biographical. *1 hr.*

209. **Some cartoons of van't Hoff.** MACKEE. **15,** 192–3 (1923). *½ hr.*

210. **Dalton Memorials in Manchester, England.** THORBURN. **16,** 190–1 (1924). Pictures and anecdotes. *½ hr.*

211. **The romance of carbon.** LITTLE. **18,** 444–51 (1926). Fascinating resumé. *2½ hrs.*

212. **Industry finds a new tool—X-rays.** KILLEFFER. **18,** 577 (1926). Study of metals, ceramics, atomic structure. *1½ hrs.*

213. **The Trona enterprise.** ROBERTSON. **21,** 520–4 (1929). Engineering problems in working Searles Lake for borax and potash. See reference 206. *1½ hrs.*

214. **Chemistry in incandescent lamp manufacture.** BARTLETT. **21,** 970–3 (1929). Tungsten filaments; frostings. *1 hr.*

215. **Development of the synthetic ammonia industry in the United States.** CRANE. **22,** 795–9 (1930).

216. **Sodium.** GILBERT *et al.* **25,** 735–41 (1933). Chemical review, indicating uses and research problems. *1 hr.*

217. **Traces from tons.** METZGER. **27,** 112–6 (1935). Rare gases; production and uses.

218. **Light metals and their alloys.** CORSE. **27,** 745–51 (1935). Interesting resumé, with pictures.

219. **Precious metals as materials of construction.** **27,** 751–5 (1935). Platinum metals; gold; silver; interesting technical details.

220. **Sugar industries of the U. S.** **27,** 989–95 (1935). Historical; technical.

221. **Columbium and tantalum.** BALKE. **27,** 1166–9 (1935). Metallurgy and industrial uses. Also **30,** 251–4 (1938).

222. **Economics of the aluminum industry.** FRARY. **28,** 146–52 (1936). Interesting technical and economic discussion.

223. **Magnesium compounds from ocean water.** CHESNY. **28,** 383–90. Technical.

224. **Rayon industry.** BENGER. **28,** 511–16 (1936). Economic and technical aspects.

225. **The soybean.** BURLISON. **28,** 772–7; 898–906 (1936). Source; uses; bibliography.

### REFERENCES FROM THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY (CONTINUED)

226. **Tailoring the long molecule.** ELLIS. 28, 1130–1144 (1936). Polymerization; cellulose; hydrocarbons; rubber; plastics; oils; proteins.

227. **Chemical symbols.** 28, 1203 (1936). A plate of alchemistic signs.

228. **Alloys.** 28, 1366 (1936). Technical discussion of alloys of chromium, nickel, copper, aluminum, silver, gold, tantalum, platinum, and other metals.

229. **Beryllium-copper alloys.** SILLIMAN. 28, 1424 (1936). Technical; chemical and physical properties of the alloys.

230. **Concentrated fertilizers.** LANDIS. 28, 1470. History; early fertilizers; modern potash, nitrate, phosphate fertilizers.

231. **From the periodic table to production.** MIDGLEY. 29, 241–4 (1937). Perkin medal address; fascinating account of Midgley's development of antiknock gasoline and of $CCl_2F_2$ refrigerant.

232. **The beri-beri vitamin.** WILLIAMS. 29, 980–4 (1937). Isolation; structure; synthesis; uses.

233. **Man-made molecules.** MIDGLEY. 30, 120–2 (1938). Antiknock gasoline; $CCl_2F_2$ refrigerant; table of man-made molecules.

234. **Raw materials of the plastic industry.** ESSELEN and BACON. 30, 125–30 (1938). Technical resumé of ingredients in many plastics.

235. **The quest for hard materials.** TONE. 30, 231–242. Perkins Medal address on abrasives and refractories; many X-ray pictures and photomicrographs.

236. **Newer developments in beryllium.** SAWYER and KJELLGREN. 30, 501–5 (1938). Metallurgy; copper alloys; bibliography.

237. **Chemistry of cellulose derivatives.** CONAWAY. 30, 516–23 (1938). Advanced resumé of esters and ethers.

238. **Indium.** LAWRENCE and WESTBROOK. 30, 611–4 (1938). Review of the chemistry of indium; bibliography.

239. **Fiber glass.** PLUMMER. 30, 726–9 (1938). History; process; properties of glass strands.

240. **The sulphur industry.** MASON. 30, 740–6 (1938). Early and recent processes. Also *ibid.*, 746–758.

241. **Less familiar elements in ceramic pigments.** HARBERT. 30, 770–2 (1938). Ti; Zr; Sn; Ce; V; Se; U; rare earths.

242. **Beginnings of the helium industry.** 30, 845–52 (1938). Discovery and development in Kansas; processes; uses.

243. **Potash.** 30, 853–92 (1938). Symposium on deposits and technical treatment; advanced.

244. **What's new in phosphorus?** KILLEFFER. 30, 967–72 (1938). Chemistry of production; costs; uses.

245. **Motor fuel economy of Europe.** EGLOFF. 30, 1091–1104 (1938). Substitute motor fuels; costs and other statistics.

### REFERENCES FROM THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY (CONTINUED)

246. **Paper goes South.** KILLIFFER. 30, 110–5 (1938). Herty pine; Kraft process; economics.

247. **An early chapter in argon production.** LANDIS. 31, 240–7 (1939). Historical and technical accounts; Perkin Medal address.

248. **Strategic raw materials.** VAN ANTWERPEN. 31, 520–30 (1939). Economic analysis of U. S. minerals and other vital materials.

249. **Plastics.** WEITH. 31, 556–62 (1939). History of various plastics; the companies producing them; little chemistry.

250. **Textile fibers.** ALEXANDER. 31, 630–42 (1939). Advanced discussion of properties; formulas; X-ray pictures; photomicrographs.

251. **Rubber.** 31, 1190–1217 (1939). Articles on history, processes and uses of rubber; discussion of its impact on research.

252. **Is chemical industry ready?** 32, 1152–80 (1940). Short resumés of preparedness of various industries: rubber, cellulose, Nylon, coal carbonization, tin, activated carbon, camphor, manganese, nitrogen, potash, tantalum, glass, drugs.

253. **Role of the catalyst.** ADKINS. 32, 1189–92 (1940). Advanced treatment, mostly on organic oxidations and hydrogenations.

254. **Glass.** SILVERMAN. 32, 1415–8 (1940). History of old glass; some newer glasses.

255. **New textile fibers, and finishes.** 32, 1543–71 (1940). Series of articles on resin, protein-base, soybean protein, electro-coated, rayon, Nylon, Vinyon, and Fiberglas fabrics.

256. **Plant nutrient deficiency symptoms.** 33, 648–53 (1941).

257. **Nutritional restoration and fortification of foods.** 33, 707–22 (1941). Vitamin and mineral content of cereals; national nutritional program.

### REFERENCES FROM CHEMICAL AND METALLURGICAL ENGINEERING

(Formerly Electrochemical and Metallurgical Industry.
Reading time is indicated for each article.)

301. **Pioneers of electrochemistry.** Charles M. Hall: 1, 10 (1902). Acheson: *ibid.*, pg. 90–1. Ostwald *ibid.*, pg. 451–2. Castner: *ibid.*, pg. 121. *1 hr.*

302. **Presentation of Perkin Medal to Dr. Charles Martin Hall.** 9, 69–72 (1911). Personal reminiscences by Hall; also by Heroult. *1½ hrs.*

303. **Perkin Medal to Herman Frasch.** 10, 73–82 (1912). Frasch's own account of how he developed the process. *3 hrs.*

304. **Synthetic ammonia.** 11, 211–4; 172–4 (1913). A technical account, by Haber himself, of experiments which led to his process. *1½ hrs.*

## REFERENCES FROM CHEMICAL AND METALLURGICAL ENGINEERING (CONTINUED)

305. **The production of salt in Szechuen Province, Western China.** **16**, 32–40 (1917); also **17**, 225–6; 313–6 (1917). Brine wells made of bamboo pipe, 4000 feet deep. *3 hrs.*

306. **The role of colloids in chemical processes.** **19**, 630–2 (1918). Colloids in ceramics, metallurgy, soap, rubber, milk, foods, etc. *1 hr.*

307. **Pictorial account of the cotton-oil industry.** WESSON. **22**, 465–72 (1920). From cotton to cotton-oil in 54 pictures. *1½ hrs.*

308. **Pure metallic arsenic.** JONES. **23**, 957–60 (1920). Production and properties. *½ hr.*

309. **Engineering problems in dust explosion prevention.** PRICE. **24**, 29–32; 473–5; 737–40 (1921). Explosions of flour, cork and other dusts; their prevention. *2½ hrs.*

310. **The dependence of the lime industry upon nature and science.** **25**, 149–52 (1921). LITTLE. Calcium carbonate in nature; a fascinating resumé of the lime industry. *1 hr.*

311. **The chemistry, manufacture and uses of nitrocellulose.** SCHLATTER. **25**, 281–6 (1921). Early history and processes. *2 hrs.*

312. **The manufacture of nitroglycerine.** SYMMES. **25**, 831–4 (1921).

313. **Synthetic ammonia by the Claude process.** **28**, 498–501 (1923). Advantages of this process over the Haber process; technical. *1 hr.*

314. **Manufacture of activated carbon.** RAY. **28**, 977–82 (1923). Variation of properties of different activated carbons. *2 hrs.*

315. **Production and uses of refined sulfur.** NEWHALL. **31**, 144–9 (1924). Forms of sulfur used industrially as fertilizers, insecticides, and preservatives. *2 hrs.*

316. **Sulfur an industrial necessity.** LINT. **32**, 365–9 (1925). Economic discussion on the uses of sulfur. *1½ hrs.*

317. **Highly developed technique required to purify gases for "Neon" signs.** O'NEILL. **35**, 143–4; 410–1 (1929). *½ hr.*

318. **High explosives.** LAMOTTE. **36**, 460 (1929). Types, chemical composition and manufacture. *1 hr.*

319. **Sightseeing at Corning.** **39**, 310–3 (1932). Story of Pyrex and its manufacture. *1 hr.*

320. **Carbon dioxide in industry.** JONES. **40**, 76–0 (1933). Refrigeration; as an explosive; hardening steels with Dry Ice. *1 hr.*

321. **March of electrochemistry.** MANTELL. **40**, 120–1 (1933). A pictorial chart covering the period 1800–1932. *1 hr.*

322. **Oceans of raw materials for magnesium compounds.** MANNING. **43**, 116–20 (1936). Industrial details of magnesium from sea-water.

323. **Carbon black for the process industries.** DROFIN. **43**, 139–42 (1936). Production processes; uses.

### REFERENCES FROM CHEMICAL AND METALLURGICAL ENGINEERING (CONTINUED)

324. **How soybeans help build Fords.** TAYLOR. 43, 172 (1936). Engineering details; some general material. See also, 43, 184 (1935).

325. **CO as a chemical raw material.** KRASE. Technical; use in metallurgy; use in the production of organic compounds.

326. **Consumption tables.** 44, 66–99 (1937). Examine statistics at the heading of each article showing what plastics, rubber, textile, etc., consumed and what it produced.

327. **Paper making at Savannah.** LEE. 44, 356–359 (1937). Engineering processes; many photographs.

328. **Radium recovery.** POCHON. 44, 362–5 (1937). Chemical steps in concentration of radium in Canada; many pictures.

329. **Acrylic resins.** FREDERICK. 44, 468–71 (1937). Properties; industrial applications. See lists of plastics, *ibid.*, pp. 427–29; 490–92.

330. **Phosphorus for progress.** KIRKPATRICK. 44, 643–50 (1937). Details of Monsanto plant.

331. **How glass bricks are made.** LEE. 45, 184–5 (1938). Brief.

332. **Flotation, etc.** 45, 268–80 (1938). Several rather advanced technical articles on ore concentration by flotation, magnetic separation, setting, and electric precipitation.

333. **Cellulose acetate by Hercules.** LEE. 45, 404 (1938). Engineering design.

334. **Electrochemical power.** 45, 462–71 (1938). Charts and tables of U. S. power consumption.

335. **Magnesium metal and compounds.** MANNING. 45, 478–82 (1938). Technical details of extraction from sea-water.

336. **A potash industry—at last.** KIRKPATRICK. 45, 488–92 (1938). Interesting technical details.

337. **Alloys.** 45, 582–602 (1938). Series of technical articles on new alloys.

338. **Charles Goodyear.** JONES. 46, 14–16 (1939). Historical; pictured flow-sheets. **Volume 46:** 269, phosphorus; 365, alcohol; 421, porcelain; 477, contact sulfuric acid; 519, Bakelite; 629, cement; 726, paper pulp; 771, bromine. **Volume 47:** 37, hydrogen sulfide removal; 119 sugar; 183, laminated plastics; 252, cyanamid; 347, acetic acid from wood; 427, lactic acid and casein; 493, synthetic amyl alcohol and acetate; 564, salt; 636, chemical stoneware; 707, alumina; 789, phenol. **Volume 48:** 108, sewage treatment; 104, sulfur mining; 108, chemical cotton; 144, sulfuric acid from petroleum sludge.

339. **How rubber is chlorinated.** LEE. 46, 456–8 (1939). Technical; brief.

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